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## TESTED IS TRUSTED

**Textile Testing**

The opening lecture was given by Mr. H. M. Taylor, M.A. (Cantab.), A.Inst.P. (British Cotton Industry Research Association) and entitled "Textile Testing." For the proper understanding of textile testing and also of the principles governing the drawing up of specifications for the final product, some understanding of statistical method is essential, said Mr. Taylor.

Among the aims of textile testing are: (1) The routine examination of raw material and the control of the processes of spinning, manufacture and finishing. (2) The inspection of goods on receipt to ensure that an agreed standard is being maintained and to reduce the possibility of substandard goods being put into service. (3) The investigation of faults in textile products to determine the origin of defects. (4) The assessment of utility and serviceability in new products.

Under (2) the principles that underlie acceptance and the drawing up of specifications were outlined and tests that characterise features of general and special importance in yarns and fabrics were discussed. Under (3) methods that can be applied to the examination of faults of the more common types in yarns and fabrics were described. Mr. Taylor concluded by saying that the assessment of utility and serviceability in textiles is one of the most difficult of the tasks of the textile technologist. Progress is being made slowly, mainly on a few specialised fronts.

FROM THE BRITISH "TEXTILE MANUFACTURER"

TEXTILE RESEARCH JOURNAL

VOL. XX, NO. 6 June, 1950

# Crystallinity of Cellulose and Its Significance for the Fiber Properties*

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**Abstract**

The subject of this paper is treated mainly from the standpoint of cotton cellulose. The concept of crystallinity is discussed not simply in the narrow sense of degree of crystallinity but in the broader sense, which involves the whole fine structure of cellulose. With respect to crystallinity in the latter sense, there are four main factors, each involving a mean value and a distribution of values, both mathematical and spatial. These parameters, independent within certain limits, are (1) the nature of the crystal lattice, (2) the percentage of crystalline material, (3) the size of the crystallites, and (4) the orientation of the crystallites. A well-planned analysis of covariance between these factors and the important physical properties of cotton would be desirable. This would be a task of considerable magnitude even if other variables not directly related to crystallinity, such as molecular size and morphology, were not active.

In the absence of such an analysis it is still possible to show the marked influence of some of these parameters on certain of the important physical properties of cotton. The relation of physical properties to the crystalline modification has been pointed out frequently by a comparison of the properties of the native fibers with those of regenerated fibers or with those of mercerized fibers. However, the changes in the percentage of crystalline material which usually occur in these transformations have not been evaluated exactly, and the conclusions drawn from previous studies should probably be checked.

Decreased crystallinity and higher content of amorphous cellulose is symbatic with increased elongation, increased moisture regain, and increased chemical reactivity. Of particular interest in the last category is the special case of hydrolysis, a reaction in which it is possible that crystallization may occur.

Data on the third parameter, the size of the crystallite, are too scanty to permit any conclusions to be drawn. A study of this factor will have to wait on improved methods for measuring the size and size-distribution of the crystalline areas.

The increase of fiber strength and of refractive index with improved orientation has been well established. A decrease in elongation usually accompanies this.

THE EXPRESSION "crystallinity of cellulose" will imply to many the degree of crystallinity of cellulose—that is, the percentage of crystallinity of the material. However, in this paper by "crystallinity" is meant the nature as well as the degree of crystallinity.

* Presented before the Textile Symposium, American Chemical Society Meeting, Atlantic City, N. J., September, 1949.

† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

The postulation of a crystalline structure for cellulose is less than 100 years old, dating back to Nägeli in 1858 [40]. The first experimental verification of crystallinity was achieved by Gilson in 1895 [11], a little over 50 years ago. The subject has been studied more and more, and, largely as a result of research within the last decade, we are beginning to have clearer ideas as to the effect of crystallinity on the physical properties of cellulosic fibers.

Without going too far into the historical aspects, let us examine what we know of the fine structure of cellulose and in the light of this knowledge define some of the terms used. Based on the painstaking research of a host of investigators, the concept has gradually arisen of the cellulose molecule as a chain of glucose residues which, in the native state, may be thousands of units long. In the textile fibers these chains orient themselves roughly in the direction of the fiber axis. In some regions the chains have reached such a high degree of order that they form crystalline regions—regions which diffract x-rays in the same manner as macrocrystals do and which show numerous other criteria of a high degree of order. These crystallites are smaller than the total length of the average cellulose molecule. This means that the same chain molecule may pass through several crystalline regions. Between these regions the chain molecule will be in a so-called "amorphous region." It must be well understood, however, that amorphous regions are not necessarily all of the same degree of order. As might be expected, there is evidence of a gradation of degrees of order between the truly crystalline regions and the regions of extremely random distribution of molecules. Nevertheless, for purposes of convenience, the cellulose chemist has fallen into the habit of dividing the fine structure of cellulose into crystalline and amorphous regions; the present author shall, for convenience, use these terms.

There are four main parameters of the fine structure of cellulose. These are (1) the nature of the crystal lattice, (2) the percentage of crystalline material (degree of crystallinity), (3) the size of the crystallites, and (4) the orientation of the crystallites. In natural materials these parameters seem to be independent of each other, although it is obvious that for extreme values there would be some dependence.

Strictly speaking, none of these parameters can be characterized simply by a single value. As is usually the case in high-polymer chemistry, we need to know not only the mean value, but the distribution of values about this mean as well. We do not as yet have much information on such distributions, so that we cannot completely evaluate their significance for fiber properties. When we consider, however, the importance that molecular-weight distribution has on the fiber properties of high polymers, it seems safe to predict that we will someday find that distribution of the crystalline characteristics has a similar importance. We may also find spatial distribution to be as important as statistical distribution in its significance for fiber properties. Van Bergen [52] has considered the effects on fiber properties of varying crystal orientation from center to rim of fiber cross section, and Elod [8] has investigated rayons with apparently different spatial arrangements of the crystalline regions.

In discussing these four aspects of the subject, examples will be drawn, where possible, from the properties of native cellulose as exemplified in cotton. In many cases, however, it will be necessary to draw examples from the other native fibers or from regenerated celluloses. Moreover, there are a great many properties for which there is little or no experimental evidence as to their relation to fine structure.

There are good reasons for such gaps in our knowledge. It would be difficult, if not impossible, to obtain a series of fibers which differ, say, only in percentage of crystalline material, or only in size of crystallite. Moreover, such a series would have to keep constant two variable properties which we have not mentioned but which greatly influence fiber properties—degree of polymerization and morphology. These two factors were not included as parameters of crystallinity in the present study, however, since they are not directly related to the subject.

In the absence of a series of fibers with only one variable, the next choice would be a well-planned statistical study of the analysis of covariance for each crystal form between the other three parameters and the important physical properties of cotton. Even this cannot readily be done at this time because of lack of methods for determining some of the parameters. It is to the task of developing such methods that much research is being devoted. Nevertheless, there is a certain amount of information about some of the relationships which exist between fine structure and physical properties which is presented herein.

### Nature of the Crystal Lattice

For the purposes of this investigation the nature of the crystal lattice has been designated as the first parameter. Four crystalline modifications of cellulose are known. Cellulose I (or native cellulose) is the modification found in the natural cellulosic textile fibers. Cellulose II (or cellulose hydrate) is the form present in regenerated cellulose or mercerized cellulose. Cellulose III [23] is a modification produced by the carefully controlled splitting off of ammonia from ammonia-cellulose; this form is very similar to Cellulose II. Cellulose IV [25, 30] is produced by heat treatments of swollen cellulose. It is so similar to Cellulose I that it was not at first recognized as a separate modification. Neither Cellulose III nor Cellulose IV has been as well characterized as the first two modifications.

In native fibers the crystalline portion is usually considered to be pure Cellulose I. Although Kubo [35] considers Cellulose IV to be present to varying extents in some natural fibers, Hess and coworkers [24] have shown that this is probably not true. In regenerated fibers and in mercerized cotton there may be varying amounts of Cellulose I and Cellulose II. If these fibers have undergone heat treatments Cellulose IV may also be present. To the best of the present author's knowledge 100% Cellulose IV has not been prepared, and Cellulose II and Cellulose III are not always free of other modifications.

The effect of crystalline modification on the physical properties has long been recognized in the differences between mercerized fibers and native fibers, and more recently in the differences between regenerated fibers and native fibers. However, these fibers differ in respects other than crystalline modification. The regeneration processes are usually accompanied by a decrease in chain length. In addition to this, both mercerized fibers and regenerated fibers will have varying percentages of crystalline material and varying degrees of orientation, depending upon the conditions of mercerization or regeneration. These accompanying changes have not been considered in many of the previous comparisons, and the conclusions drawn from previous studies should probably be checked. Valko [51] has given some cogent reasons for the opinion that the change in properties produced by mercerization are not due to the presence of Cellulose II. However, Hermans and Weidinger [18] have since demonstrated one very important property which is characteristic only of Cellulose II—the ability of the crystallite itself to absorb water—and this is a property which may well affect others.

The work of Hermans and Weidinger [15, 19] on the differences between Cellulose II and Cellulose IV deserves mention here. They transformed the former modification into the latter under conditions carefully controlled so that at least the orientation of the crystallites was constant. The change was incomplete (about 50%, although they reported a transformation of ramie to the extent of 86.7% [19]), with no appreciable change of density but with marked increase in double refraction. Since there is evidence, however, of an increased percentage of crystalline material and no data on possible changes in degree of polymerization, we cannot be too sure of the real course of the changes observed.

### Percentage of Crystalline Material

Our second parameter, the percentage of crystalline material or degree of crystallinity, is the one which has had the most attention during the past decade. Many methods have been proposed for evaluating this factor. No attempt will be made here to give a complete evaluation of all of these methods. Many of them are indirect, and the fact that they have been proposed indicates how closely some of the properties of fibers correlate with the percentage of crystallinity. For the purposes of this discussion it will be best to use as a yardstick the direct measurement of crystallinity from x-ray diagrams. Various methods have been proposed for this [20, 32], that used by Hermans and Weidinger having been applied to a large number of fibers. As will be shown, a low degree of crystallinity is symbatic with increased extensibility, increased moisture regain, decreased density, and increased chemical reactivity. Many of these properties have been suggested as the basis of methods for determining the degree of crystallinity.

The change of properties with degree of crystallinity has been measured frequently on regenerated fibers [14, 15, 31], but, as already emphasized, examples in this paper will be drawn from cotton and other native fibers. In these fibers, the degree of crystallinity is remarkably constant. However, the work of Segal, Nelson, and Conrad [46] on changing the degree of crystallinity of the cotton fiber by treatment with aliphatic amines has made it possible to prepare a series of fibers of native cellulose which dif-

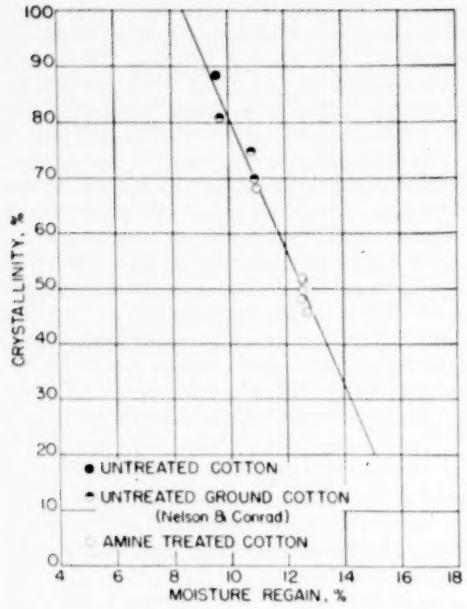


FIG. 1. *The relationship of the crystallinity of amine-treated and other samples to the moisture regain of the samples at 81% relative humidity* [40].

fer in degree of crystallization. We believe we have not introduced any great changes in orientation, but there is evidence of reduction of crystallite size and of degree of polymerization. The physical properties of such a series are still being investigated. We have, however, shown that yarns from cottons of decreased crystallinity do have increased elongation as compared with that of the original cotton (Table I). The increased moisture regain of these materials is consistent with what has already been learned with regenerated celluloses. Moisture regain is so consistently dependent upon degree of crystallinity that its determination has been considered as a method for the determination of this parameter, although Hermans points out that it can only be a first approximation [16]. It is an indirect method, but it is rapid and convenient. A few anomalous results have been reported for the relationship of moisture regain to degree of crystallinity, but in general the correspondence is high. Figure 1 shows the relationship of moisture regain to degree of crystallinity for a series of cottons studied in our laboratory, including some treated by the amine method of Segal and coworkers [46].

Closely related to the moisture regain is the heat of wetting, for which the same relationships are observed. Although we have no results for a series of fibers which vary only in degree of crystallinity, the heats of wetting for typical cellulose fibers, compiled from the results of Rees, whose paper also gives a review of the literature [44], are given in Table II.

It is obvious that the density of crystalline cellulose must be higher than that of cellulose of any of the degrees of order which we call amorphous. Amorphous cellulose may have a different density, depending upon how disordered the molecular chains are. Hermans [17], by means of analogy with other amorphous materials, has estimated a specific volume of 0.668, which would correspond to a density of 1.497, on the assumption that the density of the amorphous cellulose is approximately the same in all fibers. He has obtained close correlation between the degree of crystallinity as determined by density measurements and as determined by other physical methods (Table III). If we admit that the network

TABLE I. EFFECT OF AMINE TREATMENTS ON COTTON YARNS

| Treatment | Degree of crystallinity * (%) | Elongation (%) |
|---|---|---|
| Bleached and kiered 20/1 yarn, untreated control | 91.0 | 5.4 |
| Treated with ethylamine, followed by water boil ½ hr. | 74.2 | 13.0 |
| Treated with ethylamine, followed by water boil 2 hrs. | 58.7 | 12.3 |
| Treated with ethylamine, followed by hexylamine | 37.2 | 16.0 |

* Determined by hydrolysis method [43].

TABLE II. HEATS OF WETTING AT 0% MOISTURE REGAIN

| Fiber | Heat of wetting (cal./g.) | Degree of crystallinity [21] (%) |
|---|---|---|
| Cotton | 11.0 | 70 |
| Cotton, mercerized with tension | 17.5 | 47* |
| Cotton, mercerized without tension | 18.4 | |
| Fortisan | 22.9 | 42 |
| Viscose | 25.2 | 40 |
| Durafil | 20.4 | 40 |
| Tenasco | 22.9 | 40 |

* Mercerized ramie.

theory of cellulose structure as outlined is correct, it is impossible that there should be an exact division between crystalline and amorphous cellulose or between different degrees of amorphous cellulose. Therefore, Hermans' observations must mean that the mathematical distribution of density in the amorphous regions is approximately the same for all cellulosic fibers, a rather surprising result.

It is precisely upon the degree of crystallinity that the chemical reactivity depends. It is the amorphous region of the cellulose fiber which is the reactive region; although we would expect reactivity to be a function of the degree of crystallinity, Hermans [20] is probably correct in stating that this correspondence is not exact enough in order for chemical methods to be as accurate measures of crystallinity as physical methods are. The terms "accessible" and "nonaccessible" regions are usually more nearly correct in a discussion of chemical reactions than "amorphous" and "crystalline" regions are. There are two reasons for making such a distinction. First, not only are the amorphous regions accessible; the crystallite surfaces are also. The second reason is more complex. If amorphous cellulose consists of a continuous spectrum of regions of varying degrees of disorder, then the spaces between chains will be larger in some portions of the amorphous region than in others. In some cases there will not be room enough for very large molecules to enter, so that certain amorphous regions will not be accessible to molecules larger than a certain size. One corollary to this is that accessibility to small particles, such as water or hydrogen ion, will be greater than accessibility to large molecules, such as acetic anhydride. Another corollary is that accessibility will vary with the medium. One would expect lower accessibility with a nonaqueous, nonswelling medium. That this is true has been borne out by the results of Assaf, Haas, and Purves [1], who used nonaqueous thallous ethylate

TABLE III. DENSITY OF CELLULOSIC FIBERS (BONE DRY)

| Fiber | Density | Degree of crystallinity [21] (%) |
|---|---|---|
| Ramie | 1.550–1.556 | 70 |
| Cotton | 1.545–1.547 | 70 |
| Ramie, mercerized with tension | 1.543 | 47 |
| Ramie, mercerized without tension | 1.526 | |
| Viscose rayon | 1.518–1.525 | 40 |

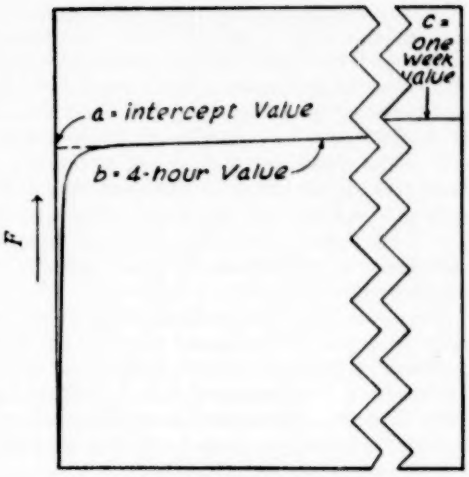


FIG. 2. *Generalized reaction curve for cellulose and characterization values for accessibility [10]. F = extent of reaction.*

as the reactant and whose values for accessibility are the lowest which have been obtained by using a chemical method. The effect of solvent is eliminated by extrapolation to zero molecular volume.

Most other chemical methods for determining accessibility make use of aqueous solutions and hence give higher values because of the swelling of cotton in water. Of these, the method yielding values most nearly in accord with x-ray determinations is that of Frilette, Hanle, and Mark [10], which involves the rate of exchange of cellulose with heavy water. The evaluation of the results is similar to that used for most of the other chemical methods. The reaction curve consists of two parts, a very rapid reaction followed by a slower and more uniform reaction. The usual explanation for this is that the more accessible material reacts rapidly while the crystalline material reacts very slowly. The latter part of the curve is linear owing to the uniform reaction of the crystalline material. If this portion of the curve is extrapolated back to the ordinate, the reaction of the crystalline (nonaccessible) material may be subtracted from the total, which gives a measure of the accessibility. This intercept value, $a$, is used in some of the methods to be discussed later; Frilette, Hanle, and Mark use the 4-hour value $b$, illustrated in Figure 2.

Another chemical method which has been studied in connection with crystallinity is the periodic-acid oxidation. This reaction also has a rapid component and a slow, linear component, and the ordinate intercept produced by extrapolating the linear portion of the rate curve is used to measure accessibility. The results of this method, suggested by Goldfinger, Mark, and Siggia [12], show that accessibility to the reagent is antibatic with the degree of crystallinity. The nonaccessibility is higher, however, than the crystallinity as determined by x-ray methods, as would be expected.

The rate of hydrolysis of cellulose is also dependent upon the degree of crystallinity, but there are complications. Hydrolysis and its relationship to the fine structure of cellulose is of such interest and importance to the whole question of cellulose structure and to the behavior of both textile and nontextile cellulose that it merits a brief discussion. Several workers have studied hydrolysis with the aim of measuring accessibility or crystallinity. Nickerson and coworkers [41] determined the extent of hydrolysis by simultaneously oxidizing the glucose produced by the hydrolysis to carbon dioxide, which could be measured, a method later modified by Conrad and Scroggie [6]. Philipp, Nelson, Conrad, and coworkers [43] simply weighed acid-hydrolysis residues to study the same reaction, while Lovell and Goldschmid [36] measured loss of weight using the Nickerson reagent.

There have been two objections raised to using the hydrolysis technique in this way. One such objection is that of Pacsu [42], who has proposed a modification of the network theory, which would view hydrolysis in a somewhat different light. This hypothesis has not yet been brought into agreement with more generally accepted views of the physical chemistry of cellulose. According to Pacsu's theory, the cellulose crystallites consist of laminae rather than of single chains. These laminae consist of parallel chains which are connected every 64 glucose units by cross-links, presumably of an open-chain glucose acetal. In the accessible cellulose regions the individual chains are unstretched and disordered (Figure 3). It is very difficult to confirm or to disprove such a hypothesis experimentally, since the irregularities (cross-linkages) involved comprise such a small part of the molecule. Points which may be raised against the Pacsu hypothesis are that cellulose derivatives in solution are almost certainly single linear molecules [49] and that, if the reaction is carried out carefully, cellulose can be converted to derivatives without appreciable change in the degree of polymerization [33]. As a matter of fact, the laminar hypothesis is in considerable conflict with the entire basis of degree-of-polymerization measurements on cellulose and its derivatives, since linearity is a requisite for the interpretation of the results. If accepted, however, the hypothesis explains the initial fast rate of hydrolysis on an entirely different basis from that of the accessibility theory.

Another and more serious objection to the use of hydrolysis measurements as an estimate of the degree of crystallinity comes from the increasing evidence that in many cases acid-hydrolysis may be accompanied by the formation of new crystalline areas, as first suggested by Ingersoll [31]. In other words, the breaking of chains in the accessible regions by acid gives increased mobility to the frayed ends, which makes possible a further crystallization at the ends of the crystallites already present. This means that values for the degree of crystallinity as obtained by acid-hydrolysis may be higher than the real values if a certain amount of crystallinity is produced during the process. Evidence to this effect has been reported by a number of investigators [4, 22, 29]. Hermans and Weidinger comparing the crystallinity as determined from the x-ray diagram at various stages of hydrolysis. The present writer believes that this second objection is valid and that even though hydrolysis techniques are very useful for comparative purposes, recrystallization should be considered in the interpretation of the results.

In spite of such objections to the hydrolysis method there is an over-all agreement between the results and those for the degree of crystallinity as measured by physical methods. Samples are at least ranked in the same order. It should also be mentioned that recrystallization in native textile fibers is less than in regenerated fibers. In fact, Hermans and Weidinger [22] found no evidence of recrystallization in the

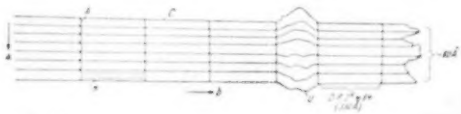

FIG. 3. *Proposed structure of native cellulose: a lamina in the a, b plane.* C = *crystalline (stretched) portion (80%).* U = *accessible (unstretched) region (20%).* A = *acid-sensitive acetal bonds.* H = *hydrogen bonds [42].*

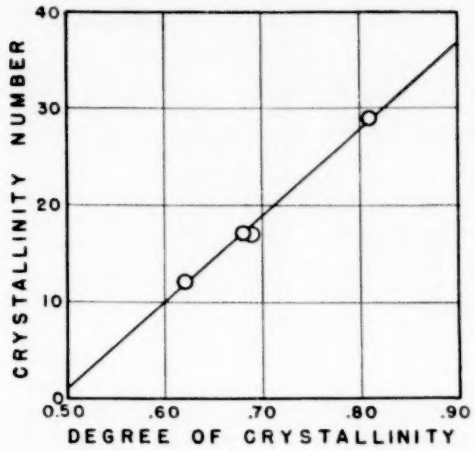


FIG. 4. *Relationship between the degree of crystallinity as determined by hydrolysis and the crystallinity number, derived from x-ray patterns [43].*

case of ramie fibers, and theirs are the only values which have been determined directly from x-ray data. At the Southern Regional Research Laboratory, we continue to use the hydrolysis method for comparative purposes.

Even for rayons, the data show a linear relationship to exist between degree of crystallinity as determined by the acid-hydrolysis method and Conrad and Scroggie's [6] "crystallinity number," derived from x-ray diagrams (see Figure 4).

Table IV gives a comparison of degrees of crystallinity as obtained by various methods. These data are the values tabulated by Howsmon [29], with two blanks filled in from later work of Hermans and Weidinger [21]. For reasons already indicated, the absolute values as obtained by different methods do not agree, but the general correspondence is enough to indicate the relationship between the factors studied.

The values for the calorimetry method given in Table IV indicate still another property which varies with the degree of crystallinity. Magne, Portas, and Wakeham [37], in their studies of nonfreezing water in fibers, determined the amount of water bound in the noncrystalline regions. From this they calculated the crystalline fraction; these are the figures cited by Howsmon [29].

## Size of the Crystallites

Data on the third parameter, the size of the crystallites, are also too scanty for drawing many conclusions. Methods for measuring size and size-distribution of either the crystalline or the amorphous regions are not too satisfactory. From x-ray diffraction data the minimum length of the crystallite is known to be about 660 Å. The other dimensions are better known, being between 50 Å. and 100 Å. [13]. There is need for a method of determining the length of the crystallites. The use of small-angle x-ray scattering for this purpose has been suggested [9, 28, 34].

There is a possibility that the degree of polymerization of limit hydrocellulose would measure this length. In order to understand this concept of limit hydrocellulose let us consider hydrolysis again. As the heterogeneous hydrolysis of cellulose proceeds, the degree of polymerization decreases. However, as has already been stated, the rate of hydrolysis slows down and when slow hydrolysis (interpreted as hydrolysis of the crystalline residue) is reached we find that it is not accompanied by any further decrease in degree of polymerization [2, 7, 45, 50, 53]. This is interpreted as meaning that the hydrolyzed chains are being stripped from the sides of the crystallite and dissolved, so that the length of the crystallite does not change with further hydrolysis. Roseveare, Waller, and Wilson [45] have interpreted the limiting degree of polymerization as representing the length of a chain passing through one crystalline and one amorphous region. This would imply practically complete recrystallization of the amorphous areas, or indicate a slow reaction of the fringed ends. In native fibers, where recrystallization, if any, appears to be very slight, it seems reasonable to consider the

TABLE IV. PERCENTAGE OF CRYSTALLINE CELLULOSE

| Method | Cotton | Wood pulp | Mercerized cotton | High-tenacity rayon |
|---|---|---|---|---|
| Hydrolysis method | | | | |
| Nickerson [41] | 94 | 90 | 89 | 79 |
| Conrad and Scroggie [6] | 92–94 | 88–91 | 85–89 | 69–73 |
| Philipp [43] | 88 | — | 82 | 67 |
| X-ray diffraction [20, 21] | 69 | 65 | 47* | 39 |
| Density [15] | 58 | 53 | 40 | 24–32 |
| Calorimetry [37] | 87 | — | 77 | 52 |
| Deuterium-oxide exchange [10] | 78 | 63 | — | 20 |

* Mercerized ramie.

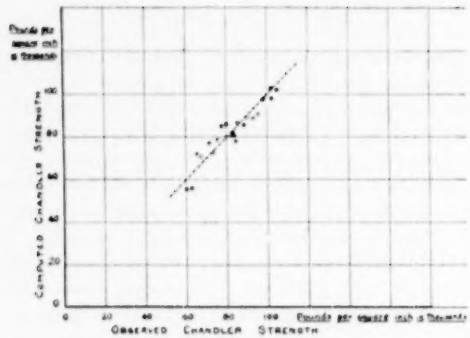


*FIG. 5. Relationship between tensile-strength values computed from x-ray diffraction-pattern measurements and observed Chandler strength values [47].*

limiting degree of polymerization as indicative of the crystallite length. Obviously, any recrystallization which occurs during acid-hydrolysis will increase the apparent length of the crystallites. There is therefore the same problem here in interpreting acid-hydrolysis results as there was when considering degree of crystallinity. Of the distribution of crystallite size we have almost no experimental evidence.

## Orientation

Orientation may be measured by optical methods, such as the dichroism of fluorescent dyes [38], or by x-ray methods [48], using the intensity of the 002 ring at various angles to the fiber axis. The latter method gives the over-all orientation in the fiber. Under investigation at the Southern Regional Research Laboratory is a new, more rapid method of measuring this x-ray angle which will permit more thorough investigation of this structural factor.

The influence of orientation on the physical properties of the regenerated celluloses has been widely studied by many investigators [15, 31, 39]; examples are cited herein from cotton celluloses, in which the same effects occur. The most striking effect of increased orientation in cellulose is the increase in tensile strength. Sisson [47] and Conrad and Berkley [5] have studied this on a score of cottons of different varieties and growth conditions. The remarkably close correlation is shown in Table V and Figure 5. A similar effect can be observed for double refraction [15]. A decrease in extensibility is to be expected from increased orientation also. Our data

TABLE V. RELATION OF FIBER STRENGTH TO ORIENTATION [47]

| Sample No. | Observed Chandler strength (10 lbs./sq.in.) | Calculated Chandler strength (10 lbs./sq.in.) | X-ray diffraction (degrees) | Dichroic orientation (%) | Cuprammonium fluidity (recip. poises) |
|---|---|---|---|---|---|
| A | 111.9 | 109.0 | 24.2 | — | — |
| 11 | 105.0 | 111.1 | 23.2 | 18.8 | 3.50 |
| 57 | 92.2 | 96.0 | 30.5 | — | — |
| 775757 | 92.0 | 88.6 | 34.1 | 16.3 | 3.54 |
| 68 | 84.4 | 85.4 | 35.6 | — | — |
| 16 | 84.0 | 79.4 | 38.5 | 8.0 | — |
| 31 | 82.7 | 81.8 | 37.3 | 5.6 | 3.62 |
| 789031 | 80.0 | 81.5 | 37.5 | 8.2 | — |
| 54 | 72.9 | 71.0 | 42.6 | — | 3.92 |
| 26 | 71.9 | 70.2 | 43.0 | 6.0 | 4.14 |

on this, however, are scant, since it is only recently that we have been able to make satisfactory elongation studies on single cotton fibers. The effect has been demonstrated on regenerated cellulose (Figures 6 and 7) [31].

The data on the effect of orientation do not require much correction for the influence of other variables. They were obtained on cottons, and, as we have already seen, all native fibers have the same crystalline modification. We have found the percentage of crystalline material in cotton to be fairly constant, regardless of variety or growth conditions. There is no satisfactory method for measuring the size of the crystallite, but the limiting degree of polymerization, which can be assumed to be a rough measure of crystallite size, does not vary greatly in the results of various investigations with different cottons. While Hessler and coworkers [26] have shown that differences in degree of polymerization of cotton cellulose correspond to varietal and growth conditions and that there exists a correlation between degree of polymerization and strength [27], they have also shown that there is a still greater correlation between orientation (x-ray angle) and strength. There remains the over-all morphology of the samples as a possible disturbing element. The importance of morphology would be difficult to evaluate at this time. However, the Production and Marketing Administration of the Department of Agriculture has been publishing measurements of x-ray angle, a measure of orientation, for several years now. They have continued to observe the marked correlation of strength and x-ray angle. However, the regression equations are somewhat different for Sea Island, American-Egyptian, and up-

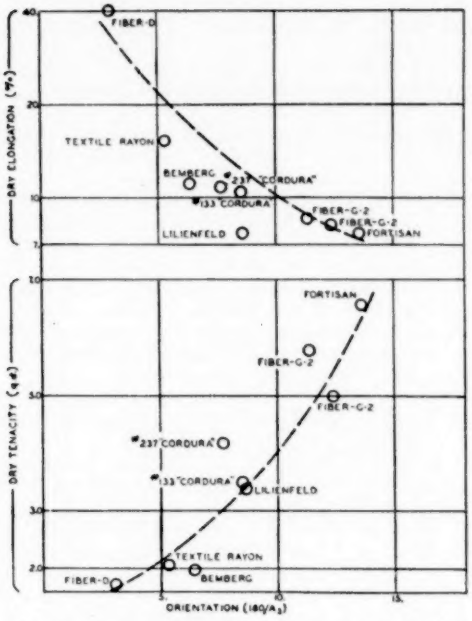


FIG. 6. *Tenacity-elongation-orientation relationship (dry) for standard rayons [31].*

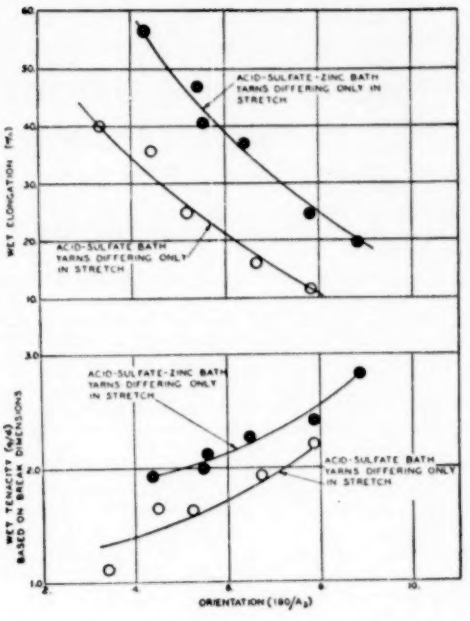
WET ELONGATION (%)
ACID-SULFATE-ZINC BATH YARNS DIFFERING ONLY IN STRETCH
ACID-SULFATE BATH YARNS DIFFERING ONLY IN STRETCH
WET TENACITY (g/d) BASED ON BREAK DIMENSIONS
ACID-SULFATE-ZINC BATH YARNS DIFFERING ONLY IN STRETCH
ACID-SULFATE BATH YARNS DIFFERING ONLY IN STRETCH
ORIENTATION (180/A₂)

FIG. 7. *Tenacity-elongation-orientation relationships (wet) for experimental rayons [31].*

land strains [3]. This difference between strains, in the absence of other data, must probably be interpreted as being due to morphological variations, but since most data on cotton are obtained for the upland varieties, we need not change any of our conclusions for this reason.

## Summary

High strength and low extensibility are associated with a high percentage of crystallinity and also with high crystallite orientation parallel to the fiber axis. High birefringence is also associated with high orientation. Moisture regain and heat of wetting decrease as the degree of crystallinity increases, whereas density increases. High chemical reactivity is definitely associated with the amorphous regions, and therefore high reactivity corresponds to a low degree of crystallinity.

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# Colloid-Chemical Basis for the Action of the Coagulating Bath upon Viscose*

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**Abstract**

In an effort to interpret the phenomena which occur when viscose solution is extruded into the spinning bath, as in the viscose rayon process, the stability of cellulose xanthate sol in the presence of electrolytes has been studied. Coagulation values for various salts and mixtures of salts on cellulose xanthate are reported. From these values a classification of ions according to their coagulating power and mechanism of coagulation has been suggested. In similar fashion, the behavior of salt mixtures on cellulose xanthate sol has been classified as additive, sensitizing, or antagonistic in accordance with colloid-chemical theory. The rate of coagulation by different ions and the influence of the degree of sulfidity and the degree of polymerization of the cellulose xanthate on the coagulation values are discussed. These data can be correlated with changes which take place in the course of fiber formation during viscose rayon spinning.

IN THE INFANCY of the rayon industry, viscose solution was extruded into a concentrated solution of neutral salts and coagulated in the form of fine filaments of water-soluble cellulose xanthate. These filaments were rendered insoluble by decomposition of the cellulose xanthate to hydrate cellulose in a second bath containing a mineral acid. The complete process then consisted of two distinct steps: (1) coagulation of cellulose xanthate and (2) regeneration of this material to cellulose itself. This two-bath system was abandoned with the advent of the Müller bath [5], which combines both these processes in a single-bath treatment. The main constituents of this bath as it is commonly used today are sulfuric acid, zinc sulfate, and sodium sulfate. Although it appears that this bath produces rayon filaments of hydrate cellulose in a single reaction, it is apparent that both processes involved in the original two-bath process must still occur either simultaneously or in some definite, relative succession, depending upon the bath composition.

In this work the spinning process as a whole has been considered as a sequence of simpler processes which can ultimately be reduced to the precipitating action of the ions present in the spinning bath on the sodium cellulose xanthate in viscose. This individual effect has been studied by measuring the coagulating power of various electrolytes on cellulose xanthate sol prepared by purification of viscose solutions, and a preliminary analysis of the mechanisms involved in the actual spinning procedure has been attempted on the basis of these coagulation data, together with other data involving coagulation rate, the degree of substitution, and the D. P. of the cellulose xanthate.

## Method

### *Isolation of Cellulose Xanthate*

An aged alkali cellulose (D.P. 270) was xanthated and an 8% solution in 6% sodium hydroxide was prepared by the usual viscose procedures. This viscose was extruded from a nozzle 2 mm. in diameter into 0.25*N* methanol-acetic acid, and the coagulated cellulose xanthate was washed with pure methanol until it was neutral to litmus paper, then washed with ether, and finally dried in a vacuum desiccator to an approximately constant weight. A stock solution consisting of 1% cellulose xanthate in distilled water was used in the determination of the coagulation values.

* For the microscopic and submicroscopic analysis, refer to Literature Cited [2].

TABLE I. COAGULATION VALUES FOR VARIOUS CHLORIDES AND SULFATES FOR 0.03% SODIUM CELLULOSE XANTHATE SOL AT 18°C

| Cations | Chlorides: Coagulation value (moles per liter) | Sulfates: Coagulation value (moles per liter) |
|---|---|---|
| Univalent | | |
| Li | 1.4 | 0.4 |
| Na | 1.0 | 0.8 |
| K | 0.5 | 0.4 |
| Rb | 1.3 | — |
| Cs | 0.4 | — |
| $NH_4$ | 0.5 | 0.4 |
| Ag | — | 0.0008 |
| H | 0.005 | 0.0025 |
| Bivalent | | |
| Mg | 0.9 | 1.2 |
| Ca | 0.9 | — |
| Sr | 0.7 | — |
| Ba | 0.7 | — |
| Zn | 0.005 | 0.004 |
| Fe | 0.000 | 0.013 |
| Cu | 0.0025 | 0.0025 |
| Cd | 0.0025 | — |
| Ni | 0.005 | 0.004 |
| Co | 0.003 | — |
| Hg | 0.0005 | — |
| Pb | 0.0005 | — |
| Tervalent | | |
| Al | 0.004 | 0.2 |
| Fe | 0.001 | 0.001 |
| Ce | 0.04 | — |
| Au | 0.007 | — |
| Quadrivalent | | |
| Th | 0.00025 | — |

*Coagulation Value*

The coagulating power of various electrolytes for cellulose xanthate sol was determined as follows: Water and a stock solution of the desired electrolytes were mixed in test tubes in various ratios so that the total volume was 2 ml. and the gradation in electrolyte concentration between any two tubes in the series corresponded to the sensitivity desired in the measurement of the coagulation values. The tubes were immersed in a thermostat with the temperature held at 18°C, and after temperature equilibrium was attained 2 drops of the stock solution of cellulose xanthate were added to each tube from a micropipet and mixed thoroughly by shaking. Each drop of the liquid from the micropipet weighed about 0.03 g., so that the cellulose xanthate concentration in the electrolyte solution was about 0.03%. The tubes were allowed to stand for 20 min. and then were examined visually for coagulation of the cellulose xanthate. Precipitation would normally occur over a wide concentration range, with the precipitate varying from a finely divided suspension to coarse floccules. The first appearance of a milky precipitate in the solution could not be used for a criterion of coagulation, for the visual determination of the first appearance of opaqueness in the solution is impossible. Fortunately, however, the transition of this milky precipitate to coarsely coagulated material occurs very sharply when the electrolyte concentration is increased to a certain degree. Therefore, the coagulation value of electrolytes for cellulose xanthate has been defined as that concentration of electrolyte in moles per liter at which the first visible *floccules* of cellulose xanthate are apparent in 2 ml. of approximately 0.03% cellulose xanthate solution after 20 min. at 18°C.

## Coagulation Values of Various Electrolytes for Cellulose Xanthate Sol

The coagulation values of the various metal chlorides and sulfates for cellulose xanthate sol are given in Table I. As is usual for negatively charged sols, the cation of the precipitating electrolyte is more effective than the anion, and, with the exception of aluminum,* the coagulation values of the chloride and the sulfate of the same element are of the same order of magnitude. However, as can be seen in the table, the Schulze-Hardy valency rule, which applies for many lyophobic and weakly solvated sols, is not valid for this colloidal system. All alkali and alkali-earth elements have coagulation values of the same order of magnitude, whereas silver and hydrogen ion have enormously higher coagulating power. All bivalent heavy metals have a coagulating power which is much higher than that of alkali and alkali-earth elements and of the same order of magnitude as that of several trivalent elements. Thorium chloride, the only tetravalent electrolyte studied, has a very strong coagulating power. Similarly, the lyotropic series which is apparent in the coagulation of many strongly solvated sols is not recognizable, for the coagulating power of alkali-metal cations does not change in regular order with atomic weight and the

*The hydrolysis of the aluminum salts does not account for this anomaly. Rather, the difference in the structure of solutions of aluminum chloride and sulfate should be taken into consideration. Mirlas [4] gives the coagulation values of several electrolytes whose hydrolysis is negligible.

order of coagulating power is different for chlorides and sulfates of these cations.

A significant characteristic of cellulose xanthate sol is its chemical reactivity. Namely, the sodium ion of sodium cellulose xanthate can be interchanged with the cations of coagulants. The stability of the newly produced colloidal system involving the interchanged xanthate seems to be closely correlated with the coagulation value of the precipitating agent. Thus a very regular periodicity in the coagulating power of elements can be recognized when they are arranged according to the periodic system. The elements of sub-group "a" in all periods possess a low coagulating power which seems to be independent of valence, whereas those of sub-group "b" and the transition elements possess a coagulating power many times higher. If we formulize the cellulose xanthates as follows:

$$\begin{matrix} & O-(C_6H_{10}O_5)_n \\ C & \\ & S-Me \end{matrix} \qquad (Me = \text{Metallic element}),$$

we can deduce that the bond which controls the solubility of cellulose xanthate in water should be S—Me, and that the solubility of the cellulose xanthate of an element would parallel that of the sulfide of the same element. This is apparent in the data, for elements whose sulfides are insoluble in water exert higher coagulating power upon sodium cellulose xanthate sol than elements whose sulfides are soluble in water.

On the other hand, the low coagulation values of hydrochloric and sulfuric acids arise from the fact that at low concentrations they induce the decomposition of the cellulose xanthate, regenerating highly insoluble cellulose which is immediately precipitated.

Taking these properties of ions of various elements into consideration, the following classification according to their coagulating power has been formulated for convenience in later discussion:

*Group I: Alkali and Alkali-Earth Ions.* The coagulation values of their chlorides and sulfates are of the order of magnitude of 1 mole per liter.

*Group II: Bivalent and Tervalent Ions Such as Zinc and Ferric.* Their coagulation values are of the order of 5 millimoles per liter.

*Group III: Polyvalent Ions Such as Ferrous, Aluminum, Cerium, and Thorium.* Their coagulation values range from 0.1 mole to 0.1 millimole per liter.

*Group IV: Hydrogen Ion.* Hydrogen ion is characteristic in that it induces the dissociation of cellulose xanthate into its components and has a coagulating power of a higher order of magnitude than that of elements in Group I.

### Mixtures of Two Electrolytes: Additivity

In order to approximate the conditions of actual spinning baths, which normally contain two or three different electrolytes, the study was extended to include the behavior of ion pairs in coagulating cellulose xanthate. Although no clear-cut rules for coagulation by these mixtures can be formulated, three distinct types of behavior were observed. A number of experiments have shown, without exception, that in mixtures of any two ions from Group I above the coagulating action of the two ions is additive and the relationship

$$\frac{C_1'}{C_1} + \frac{C_2'}{C_2} = 1$$

will apply when $C_1'$ and $C_2'$ are the coagulation values of electrolytes 1 and 2 in the mixture and $C_1$ and $C_2$ are the coagulation values of electrolytes 1 and 2 alone. An example of this type of behavior as exhibited by a $Li_2SO_4$-$Na_2SO_4$ mixture is illustrated in Figure 1. Similar behavior was found for thirteen other ion pairs—eight chloride pairs (Na-Li, K-Li, $NH_4$-Li, Na-K, Na-$NH_4$, K-$NH_4$, Na-Mg, and Na-

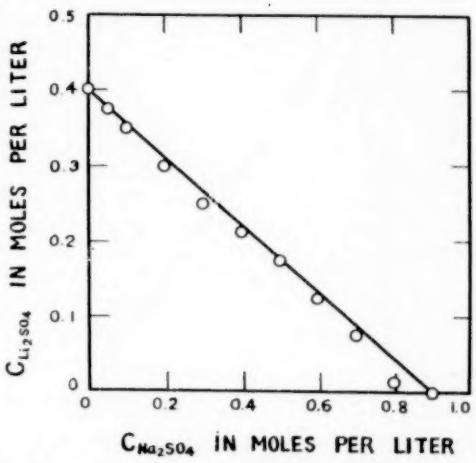


FIG. 1. *Flocculation of cellulose xanthate sol by mixtures of $Na_2SO_4$-$Li_2SO_4$.*

Ca) and five sulfate pairs (K-Li, $NH_4$-Li, Na-K, Na-$NH_4$, and K-$NH_4$).

A survey of the results shows that the additivity relationship is more dependent on the magnitude of the coagulation values for individual electrolytes than upon the valency of the cations. This holds true for mixtures containing ions of different valence as long as the coagulation values are of the same order of magnitude. Similar relationships have been recorded in the literature for several other colloidal systems, where the valency rule does apply. However, in these cases additivity does not occur for such mixtures as Na-Mg or Na-Ca.

### Mixtures of Two Electrolytes: Ion Antagonism

A very marked ion antagonism in coagulating action occurs in mixtures of the polyvalent ions of Group III and the univalent ions of Group I. This effect occurs for both chloride and sulfate mixtures, and, in accordance with the early results of Linder and Picton [3] on arsenic trisulfide sol, it becomes more pronounced as the differences between coagulation values of the individual electrolytes become greater. Thus, more than ten times the coagulation value of thorium chloride is necessary to induce coagulation when it co-exists with lithium chloride. This antagonistic effect was observed with the chloride pairs Al-Li, Al-Na, Ce-Li, Ce-Na, Th-Li, and Th-Na, and a sulfate pair, Al-Na. Figure 2 shows graphically an example of a $AlCl_3$-NaCl pair.

Ion antagonism also occurs in electrolyte pairs which involve sulfuric acid. As mentioned previously, the acid exerts anomalously high precipitating action upon cellulose xanthate sol. However, when it co-exists with metal sulfates from either Group I or Group II, its coagulating power is remarkably depressed. The experiments were conducted with the electrolyte mixtures which contain sulfuric acid and Li-, Na-, K-, $NH_4$-, or Zn-sulfate. As typical examples, the data for two mixtures, $H_2SO_4$-$Na_2SO_4$ and $H_2SO_4$-$ZnSO_4$, which are used widely in actual spinning baths, are plotted in Figures 3 and 4.

There is no generally applicable explanation for the antagonistic effect of one ion on the coagulating power of another. An approach is to consider the physicochemical condition of ions. The activity coefficients of ions of an electrolyte can be depressed remarkably by the addition of another electrolyte. Calculative computation of activity coefficients of cations in the various electrolyte mixtures explains more or less quantitatively the antagonism as ob-

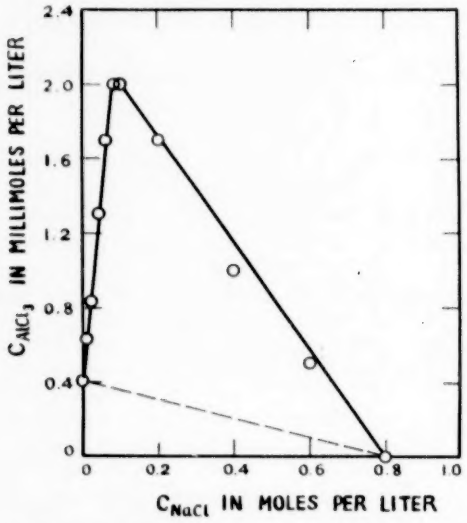


FIG. 2. *Flocculation of cellulose xanthate sol by mixtures of NaCl-$AlCl_3$.*

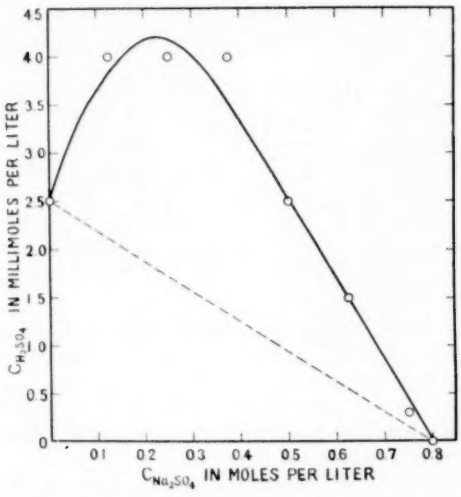


FIG. 3. *Flocculation of cellulose xanthate sol by mixtures of $Na_2SO_4$-$H_2SO_4$.*

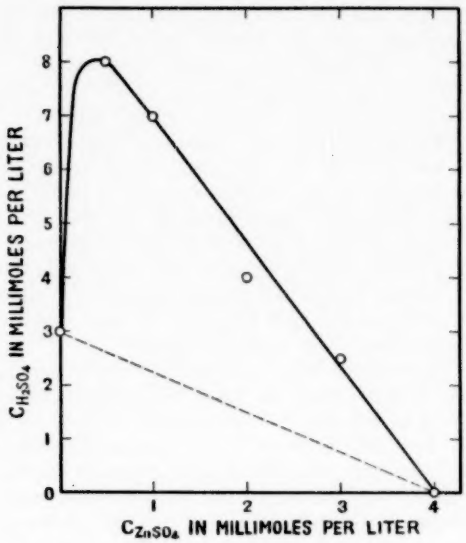


FIG. 4. *Flocculation of cellulose xanthate sol by mixtures of $ZnSO_4$-$H_2SO_4$.*

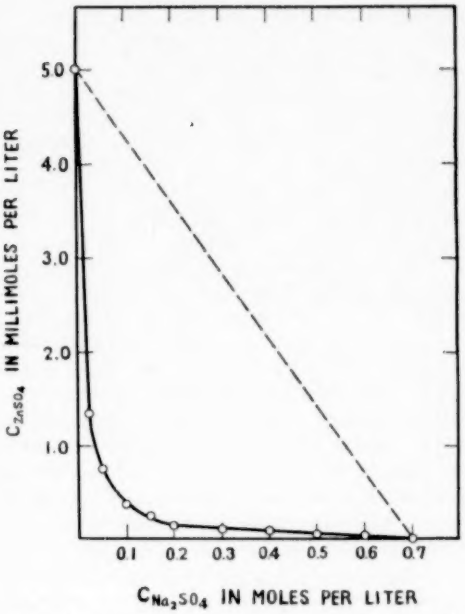


FIG. 5. *Flocculation of cellulose xanthate sol by mixtures of $Na_2SO_4$-$ZnSO_4$.*

served above, but it is not certain whether or not the ion activity uniquely controls the actual coagulation. So far as the coagulation of cellulose xanthate sol is concerned, the chemical reactivity of the sol seems to be of greater significance than the physicochemical condition of the dispersion medium (see section on Speed of Coagulation below).

### Mixtures of Two Electrolytes: Sensitization

Sensitization of cellulose xanthate toward coagulation occurs in mixtures of ions from Group I and ions from Group II. This effect is pronounced for mixtures of zinc chloride or sulfate with other metallic chlorides or sulfates and is marked by a considerable decrease in coagulation value for each component in the mixture. Later studies showed that mixtures containing ferric ion exhibit a similar effect, and in this respect zinc and ferric ions, classified as Group II, are unique among the ions studied. This sensitizing effect was observed in all experiments in which chloride mixtures of Zn-Li and Zn-Na and sulfate mixtures of Zn-Na, Zn-K, Zn-$NH_4$, and $Fe^{+++}$-Na were used. As a typical example, the results for a $ZnSO_4$-$Na_2SO_4$ mixture are shown in Figure 5.

Sensitization itself is rather unusual in colloid chemistry, but it has been observed when hydrophilic sols or non-electrolytes were added to hydrophobic sols [1]. This effect has been explained by a mutual discharge of electrically charged particles with a resulting increase in sensitivity to the electrolyte coagulants. The sensitizing effect as observed in this case seems to be controlled by the chemical reactivity of cellulose xanthate and the velocity of the reaction. As will be shown later, zinc ion reacts more rapidly with sodium cellulose xanthate than any other ion does, and it produces partially substituted zinc-sodium xanthate sol, which is more easily coagulated than the original sol. As a consequence, smaller amounts of the coagulator are needed to produce coagulation.

### Speed of Coagulation

Another important factor which must be considered in coagulation involving chemical reaction is the correlation of the speed of coagulation with the relative reaction rates of the various coagulators. To estimate the relative rates of coagulation, the

following nephelometric procedure was adopted. A small lamp fed by a 6-v. accumulator with a large capacity was employed as a light source. The coagulation vessel was a small drum provided with plane-parallel quartz plates at both ends and a wide mouth in the middle of the length. The inner diameter of the drum was 29 mm. and its length was 50 mm. The drum was placed in the apparatus so that the light axis passed through the middle of the drum lengthwise. A limiting screen with a circular opening 5 mm. in diameter was attached between lens and lamp, and the light cone was focused on the sensitive surface of a thermopile, which was placed behind the vessel and connected with a mirror galvanometer. 26 ml. of an electrolyte solution was poured into the vessel and the deflection of the galvanometer was read. Then 7 ml. of the stock solution of 1% cellulose xanthate sol was added and mixed thoroughly by quickly shaking the drum, and the galvanometer deflection was recorded as a function of time. Experiments were carried out at different electrolyte concentrations, with the concentration at which coagulation took place being taken as a standard. The results obtained with sulfuric acid and metal sulfates are shown in Figure 6. Hydrochloric acid and metal chlorides gave similar results.

From Figure 6 it can be seen that the coagulation by zinc ion is very rapid, for maximum clouding of the solution is reached within the time required for mixing. The clearing of the solution, represented by the increasing deflection of the galvanometer after reaching the minimum, is due to the sinking of flocculates which have been produced. Sodium ion affects coagulation more slowly, with 80-90% of the total change being accomplished directly after the mixing,

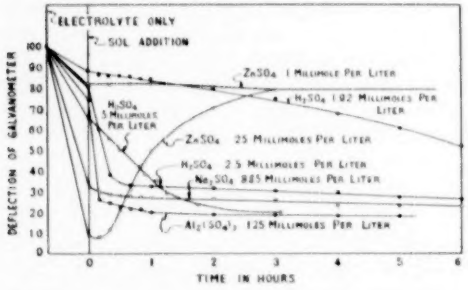
1 ELECTROLYTE ONLY
2 SOL ADDITION
ZnSO4 1 MILLIMOLE PER LITER
H2SO4 1.92 MILLIMOLES PER LITER
H2SO4 5 MILLIMOLES PER LITER
ZnSO4 25 MILLIMOLES PER LITER
H2SO4 2.5 MILLIMOLES PER LITER
Na2SO4 8.65 MILLIMOLES PER LITER
Al2(SO4)3 1.25 MILLIMOLES PER LITER
DEFLECTION OF GALVANOMETER
TIME IN HOURS

FIG. 6. *Course of coagulation caused by sulfates and sulfuric acid. Deflection is given in percent (using 100 as the reference for electrolyte only).*

whereas aluminum acts still more slowly, with the immediate change being only 30% of the total, and 1 hr. being required for complete coagulation.

The action of sulfuric acid is extremely slow when compared to that of zinc. For sulfuric acid of 1.92 millimoles per liter the immediate coagulation is negligibly small and the coagulation process progresses very slowly in the course of a long time. Even for a higher concentration, in the range 2.5 to 5.0 millimoles per liter, the immediate coagulation is very small. Although sulfuric acid and zinc sulfate are similar in their coagulating capacity, the course of the coagulation as it is induced by these two compounds seems to be markedly different.

These relative rates of coagulation may be significant in determining the actual sequence of coagulation and regeneration occurring immediately after the extrusion of viscose into the coagulating bath. In this respect, it should be noted that of the normal spinning-bath components zinc ion is the most rapid, sodium ion the medium, and hydrogen ion the slowest coagulator.

One explanation of the antagonistic effect discussed above is possible from these relative coagulation speeds. The ions of Group I react faster than those of Groups III and IV. When mixtures of ions of Groups I and III or Groups I and IV are used, component I reacts earlier than components III and IV and forms compact particles which are attacked more slowly by Group III ions (ionic interchange) or Group IV ions (radical dissociation).

### Interpretation of Actual Spinning Process

The cations have been classified into four groups according to their coagulating power and their behavior in cooperative action in mixtures:

I. $Li^+$, $Na^+$, $K^+$, $NH_4^+$, $Mg^{++}$, $Ca^{++}$
II. $Zn^{++}$, $Fe^{+++}$
III. $Al^{+++}$, $Ce^{+++}$, $Th^{++++}$
IV. $H^+$

In addition, the cations used in normal spinning baths have been classified according to their relative coagulation speeds, as follows:

| | |
|---|---|
| Rapid | $Zn^{++}$ |
| Medium | $Na^+$ |
| Slow | $H^+$ |

The cooperation of cations in mixtures of Group I ions is computed additively, while the binary combinations of cations of Group I with those of Group

II always show sensitized coagulation. Mixtures of hydrogen ions (Group IV) with cations of any other group are always marked by an antagonistic effect. Since the most important cations in the usual coagulating baths are sodium, zinc, and hydrogen, it seems quite possible that both antagonism and sensitization may play important roles in the practical spinning of viscose rayon.

In addition, it is apparent from the coagulation data that the sodium ions may be replaced by other ions assigned to Group I, and in actual spinning practice a considerable part of the sodium could be replaced by magnesium or ammonium sulfate in amounts corresponding to their relative coagulating powers, without appreciably altering the coagulation characteristics of the spinning bath. But zinc ion may not be replaced by any other ion from another group without changing the spinning conditions.

From these coagulation characteristics and the relative coagulation speeds of zinc, sodium, and hydrogen ions a working hypothesis has been formulated for the mechanism of coagulation of viscose in commercial rayon spinning. The zinc ion is probably the first to react with the cellulose xanthate after extrusion of viscose into the bath liquor. The coagulating power of zinc ion, which in itself is very strong, is strongly sensitized by the co-existing sodium ion (Figure 5). Hence a small amount of zinc sulfate is sufficient to effect a highly sensitized, rapid coagulation. Thus, very thin films of zinc-sodium cellulose xanthate are precipitated at the surface of the extruded mass, making it easy to draw out the viscose columns from the spinneret holes and to assure a constant supply of filaments into the coagulating bath.

The inner layer contiguous to this thin film is now exposed during a certain time interval to the degenerated bath liquor which consists mainly of sodium sulfate and sulfuric acid since zinc ions are rapidly consumed to form the epidermis. The action of sodium ion takes place here prior to that of hydrogen ion, and a layer, coagulated to an appropriate extent,

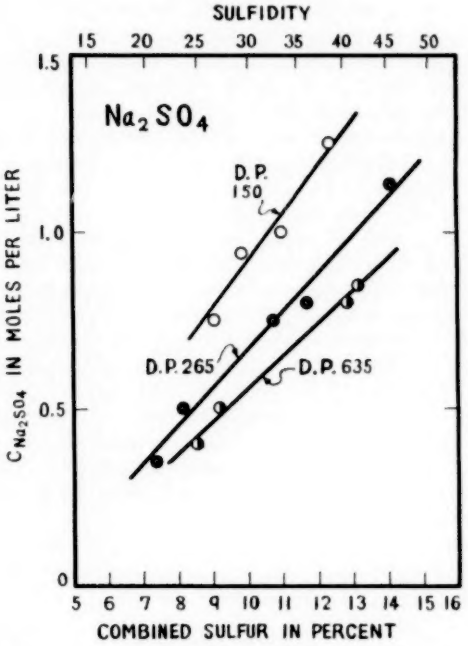


FIG. 7. *Coagulation value of sodium sulfate vs. sulfur content and sulfidity of cellulose xanthate samples of various degrees of polymerization.*

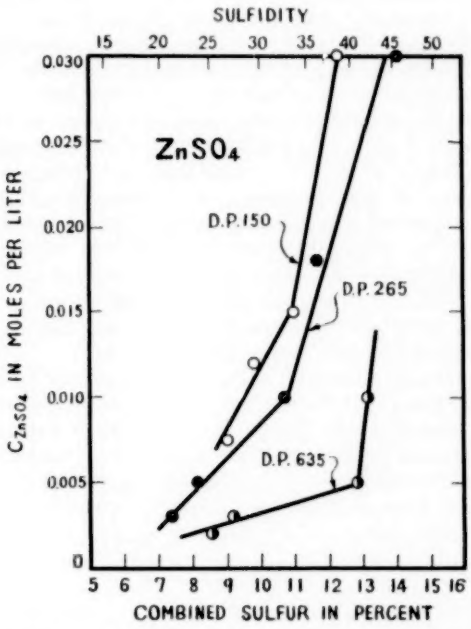


FIG. 8. *Coagulation value of zinc sulfate vs. sulfur content and sulfidity of cellulose xanthate samples of various degrees of polymerization.*

is produced which extends from the surface for a certain depth into the core of each column. This layer retards the action of hydrogen ion, and the regeneration of cellulose takes place slowly, as can be seen from the data on the antagonism phenomenon. If stretch is applied, by whatever means, when this layer is being subjected to the action of hydrogen ion, it will give rise to the axial orientation and fixation of cellulose molecules. This explains the formation of the "skin" effect in viscose rayon. Thickening of the skin with decreasing hydrogen ion, or increasing sodium and zinc ion, is compatible, within reasonable limits, with this theory.

### Effect of Sulfidity and Degree of Polymerization

In addition to these effects of the bath composition on the coagulation of cellulose xanthate from viscose, it is a well-known fact that the nature of the cellulose molecule itself is an important factor in determining the ease of coagulation and the ultimate properties of the viscose rayon yarn. For example, a ripened viscose is more easily coagulated in the spinning bath than an unripened viscose because of the decrease in the number of xanthate groups which accompanies ripening. Therefore, in the work reported here the coagulation of cellulose xanthate sols of different degrees of xanthate substitution and different chain lengths was studied. The results in Figures 7 and 8 show that, as expected from practical and theoretical considerations, the coagulation of cellulose xanthate sol becomes easier with decreasing degree of xanthation and increasing degree of polymerization of the cellulose molecules. The sulfidity ordinate used in Figures 7 and 8 is so defined that a sulfidity of 300 corresponds to cellulose trixanthate.

Increasing the temperature of the coagulation system in all cases causes a marked decrease in the coagulation values of all ions for any cellulose xanthate sample. Many other factors, such as viscose composition, especially in terms of the percent cellulose and the percent sodium hydroxide, will affect the over-all mechanism of coagulation in the spinning process and should be studied to complete the present picture.

### Summary

1. Coagulation values of various electrolytes for cellulose xanthate sol were determined. The cation of each electrolyte usually determines the coagulation value, but, in contrast to other colloidal systems, the valency rule and lyotropic series are not ascertainable. Periodicity in coagulating power can be assigned, in the sense that the elements of sub-group "a" (light metals) have coagulation values of the order of magnitude of 1 mole per liter, whereas the elements of sub-group "b" and of the transitional group (heavy metals) have coagulation values as low as $10^{-2}$ to $10^{-3}$ mole per liter. There is parallelism between the coagulation values of the elements and the solubilities of the sulfides of the elements.

2. Cations can be classified in four groups on the basis of coagulating power:

I. Alkali-metal and alkali-earth metal ions
II. Zinc and ferric ions
III. Polyvalent ions such as aluminum, cerium, and thorium
IV. Hydrogen ion

3. The coagulating action of mixtures of two electrolytes on cellulose xanthate sol shows three distinct types of behavior:

(*a*) In mixtures of any two ions in Group I, the action is always additive.
(*b*) In mixtures of ions from Groups I and III, I and IV, II and IV, or III and IV, a marked ion antagonism occurs.
(*c*) In mixtures of ions from Groups I and II a marked sensitization toward coagulation occurs.

4. Speeds of action of various electrolytes upon cellulose xanthate sol differ widely, and the result is that zinc acts at extremely high speed, sodium at moderate speed, and hydrogen at very slow speed. These differences in reaction speed may account for the occurrence of marked antagonism and sensitization which are peculiar characteristics of the coagulation of cellulose xanthate sol.

5. The changes which take place during spinning can be correlated with these coagulation data, and the course of fiber formation from viscose was interpreted from the colloid-chemical point of view.

6. The influence of sulfidity and degree of polymerization upon the coagulation properties of cellulose xanthate sol was studied.

### Acknowledgment

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# Rate of Acid Sorption by Wool Fibers

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IT HAS BEEN SHOWN that wool fibers have a surface layer, which has been called the epicuticle, with properties different from those of wool keratin [9]. It has also been suggested that this layer plays an important role in the dyeing of wool—that it is responsible for most cases of tippy dyeing, etc. [8]. In a recent investigation Millson has shown that polyvalent ions of chromium, aluminum, iron, etc., are preferentially sorbed by the tip portion of the fiber [10].

It was therefore found advisable to investigate the kinetics of one of the best-known cases of sorption by wool fibers—namely, their sorption of mineral acids. According to the Donnan theory [11], it is the hydrogen ion that is sorbed by the fiber from solutions of strong mineral acids, the anions only accompanying the hydrogen ion so as to maintain electroneutrality. If hydrochloric acid is used for the experiments, the driving force for the sorption is associated only with the hydrogen ion. This will obviously be a much less complicated type of sorption than that which takes place when dyes are used.

### Experimental Technique

For the experiments, Australian Fleece Wool 64s was used. It was buffered to pH 6.8 and rinsed several times with distilled water. All samples were extracted either with ether or with alcohol before they were measured.

The fibers were then chopped to pieces of 1–3-mm. length with a cutting device. The increase in surface area which results from this procedure is negligible. A conditioned sample of 0.6 g. was weighed out in a glass tube open at both ends and thoroughly wetted with a known amount of water. 250 ml. of HCl solution containing 5 milliequivalents per liter was measured in a beaker and the beaker was placed in a thermostat; the temperature employed in all experiments was 22.0°C. A stirrer and a conductivity cell were inserted into the solution. At zero time the sample was transferred from the glass tube to the liquid, the zero value for the concentration being corrected for the amount of water in the tube. At convenient intervals the decrease in concentration was determined by means of a Philoscope conductivity bridge, which gives the percentage value directly. The suspension of the chopped fibers did not interfere with the conductivity measurements, if care was taken not to leave any long fibers when chopping the material.

The same dispersing and chopping technique has also been employed in scouring experiments [3, 12]. In this procedure the liquid is well stirred close to the phase boundary between solution and fiber.

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Thus the liquid diffusion, which will complicate the interpretation of the results when yarn or fabric is used instead of fibers, is avoided [1, 2].

### Mathematical Treatment of Data

Typical examples of sorption curves for hydrochloric acid are given in Figure 1 (for symbols, see below). However, this method of reproducing the data is not very clear or useful and there is always an urgent need to find a mathematical relationship that will give only one characteristic value for each curve.

The sorption of a solute from solution, when the amount of solute is finite and the sorbing medium is a plane sheet or a cylinder, has been treated extensively [4–6]. The theories put forward were adopted in this case. The sorption of hydrochloric acid by the wool fibers was assumed to be linear over the short concentration range in question, and the fibers were assumed to be cylindrical. The first assumption is an approximation, but it was made in order to simplify the solution of the diffusion equation.

By solving the diffusion equation the following equation is obtained [13]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{n=\infty} \frac{4\alpha(1+\alpha)}{4 + 4\alpha + \alpha^2 q_n^2} e^{-q_n^2 \beta t}, \qquad (1)$$

where $M_t$ is the amount of solute in the fiber at time $t$, $M_\infty$ is the amount at infinite time, and $q_n$ is the non-zero, positive root in the equation

$$\alpha q_n J_0(q_n) + 2J_1(q_n) = 0, \qquad (2)$$

where $J_0(q_n)$ and $J_1(q_n)$ are Bessel functions of zero and first order, respectively.

$$\beta = \frac{D}{(R+1)a^2} \qquad (3)$$

and

$$\alpha = \frac{A}{\pi a^2 (R+1)} = \frac{B_\infty}{M_\infty}, \qquad (4)$$

where $D$ is the diffusion constant, $a$ is the fiber radius, and $A$ is the cross section of the bath, assuming the fiber to be of infinite length. $R$ is the distribution coefficient (the quotient between the concentration in the fiber and in the bath) and $B$ is the amount of solute in the bath. Equation (1) is solved for the $\alpha$ in question, and values of $M_t/M_\infty$ for different values of $\beta t$ are determined. For small values of $\beta t$, the series in equation (1) converge slowly; hence an alternative solution was derived by Crank [5]:

$$\frac{M_t}{M_\infty} = \frac{2}{\alpha}(1+\alpha)\left[\frac{2}{\sqrt{\pi}}\sqrt{\beta t} - \left(\frac{1}{2} + \frac{2}{\alpha}\right)\beta t - \frac{4}{3\sqrt{\pi}}\left(\frac{1}{8} - \frac{2}{\alpha} - \frac{4}{\alpha^2}\right)(\sqrt{\beta t})^3 \cdots\right]. \qquad (5)$$

The theoretical curve as obtained from equations (1) and (5) was plotted with $M_t/M_\infty$ vs. $t$. From this curve the $\beta t$ values, corresponding to measured values of $M_t/M_\infty$, were determined graphically. These values of $\beta t$ were divided by the corresponding values of $t$, the constancy of $\beta$ then showing the closeness of the fit of the experimental curve to the theoretical one. Examples of this calculation are

TABLE I

| $t$ (min.) | $M_t$ | $M_t/M_\infty$ | $\beta t \times 10^3$ | $\beta \times 10^3$ | $\beta t \times 10^3$ (calc.) | $M_t/M_\infty$ (calc.) |
|---|---|---|---|---|---|---|
| 1 | 3.9 | 0.256 | 11.0 | 11.0 | 11.5 | 0.262 |
| 2 | 5.1 | 0.336 | 19.9 | 10.0 | 23.0 | 0.358 |
| 3 | 6.3 | 0.414 | 32.1 | 10.7 | 34.5 | 0.426 |
| 4 | 7.2 | 0.474 | 44.6 | 11.1 | 46.0 | 0.481 |
| 5 | 8.0 | 0.526 | 57.2 | 11.4 | 57.5 | 0.527 |
| 6 | 8.7 | 0.572 | 71.0 | 11.8 | 69.0 | 0.565 |
| 7 | 9.2 | 0.606 | 81.5 | 11.6 | 80.5 | 0.603 |
| 8 | 9.7 | 0.638 | 94 | 11.7 | 92 | 0.633 |
| 10 | 10.6 | 0.697 | 120 | 12.0 | 115 | 0.687 |
| 12 | 11.3 | 0.744 | 145 | 12.1 | 138 | 0.732 |
| 14 | 11.8 | 0.777 | 166 | 11.9 | 161 | 0.770 |
| 16 | 12.3 | 0.810 | 190 | 11.9 | 184 | 0.801 |
| 20 | 13.0 | 0.855 | 232 | 11.6 | 230 | 0.853 |
| 25 | 13.7 | 0.902 | 292 | 11.7 | 288 | 0.899 |
| $\infty$ | 15.2 | | | | | |

Mean value of $\beta$ is $11.5 \times 10^{-3}$

TABLE II

| $t$ (min.) | $M_t$ | $M_t/M_\infty$ | $\beta t \times 10^3$ | $\beta \times 10^3$ | $\beta t \times 10^3$ (calc.) | $M_t/M_\infty$ (calc.) |
|---|---|---|---|---|---|---|
| 1 | 2.7 | 0.204 | 6.4 | 6.4 | 7.2 | 0.216 |
| 2 | 3.6 | 0.273 | 12.1 | 6.05 | 14.3 | 0.295 |
| 3 | 4.3 | 0.326 | 17.8 | 5.94 | 21.5 | 0.353 |
| 4 | 5.1 | 0.386 | 26.3 | 6.58 | 28.7 | 0.401 |
| 5 | 5.5 | 0.416 | 31.2 | 6.25 | 35.8 | 0.439 |
| 6 | 6.2 | 0.480 | 44.3 | 7.40 | 43.0 | 0.474 |
| 7 | 6.9 | 0.523 | 54.6 | 7.80 | 50.2 | 0.506 |
| 8 | 7.1 | 0.538 | 58.3 | 7.28 | 57.3 | 0.534 |
| 9 | 7.5 | 0.568 | 67.2 | 7.46 | 64.4 | 0.559 |
| 10 | 7.7 | 0.584 | 72.3 | 7.23 | 71.6 | 0.581 |
| 11 | 8.2 | 0.621 | 85.0 | 7.73 | 78.7 | 0.605 |
| 12 | 8.3 | 0.629 | 88 | 7.33 | 86 | 0.625 |
| 13 | 8.6 | 0.651 | 96 | 7.38 | 93 | 0.643 |
| 14 | 8.8 | 0.667 | 103 | 7.35 | 100 | 0.661 |
| 15 | 9.2 | 0.697 | 116 | 7.73 | 107 | 0.676 |
| 20 | 10.1 | 0.765 | 154 | 7.70 | 143 | 0.747 |
| 25 | 10.8 | 0.819 | 193 | 7.72 | 179 | 0.800 |
| $\infty$ | 13.2 | | | | | |

Mean value of $\beta$ is $7.16 \times 10^{-3}$

TABLE III

| Scouring method | Unextracted samples | Ether-extracted samples | Alcohol-extracted samples |
|---|---|---|---|
| Petroleum-solvent scour | 0.378 | 1.31 | 4.32 |
| Soda-soap scour | 0.973 | 1.80 | 3.52 |
| Nonionic detergent scour | 0.440 | 0.855 | 2.55 |

The figures are values of $D$ in cm.²/min. $\times 10^6$

given in Tables I and II for the curves shown in Figure 1. $M_t$ is given in percent of the original amount of solute. The theoretical values for $M_t/M_\infty$ obtained from the mean value of $\beta$ are also given and are represented by the curves in Figure 1. The values in Table II give the general trend of the deviation in $\beta$ which was encountered in the experiments. This deviation might be due to the approximation which was made and to the inaccuracy of the measurements, especially those in determining $M_0$ and $M_\infty$. From equations (3) and (4), $D$ could be calculated if the fiber radius were known, or, better, the mean value of the square of the fiber radius. The free diffusion constant for HCl in 0.01$N$ solution at 18°C is $1.61 \times 10^{-5}$ cm.²/min. (Landolt-Börnstein) and this value could be compared with those given in Tables III–V.

### Solvent Extraction of Wool Fibers

Thus when a relatively good representation of the data is available the effect of the epicuticle on the sorption of hydrochloric acid can be quantitatively evaluated. It was, however, eventually found that before this influence could be determined the wool fibers must be freed from all foreign substances which might interfere with the diffusion. This problem turned out to be a very complex one, and in this report only the first fundamental facts will be given.

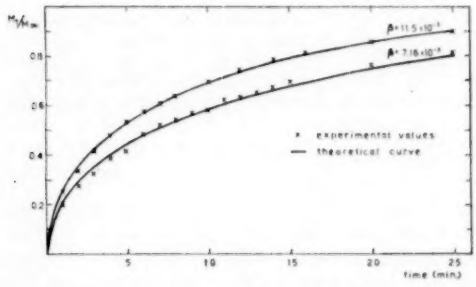


FIG. 1. *Curves showing the sorption of HCl by wool fibers.*

TABLE IV

| Treatment | $D$ (cm.²/min. $\times 10^6$) |
|---|---|
| Unextracted | 0.378 |
| Boiled in ether | 0.768 |
| Boiled in alcohol | 1.21 |

Wool top was taken from three different raw-wool scouring experiments, and each lot was divided in three parts, two of them being extracted in a Soxhlet extractor with ether and alcohol, respectively, for 3 hrs. The diffusion constant for these 9 samples was measured and the results are given in Table III.

It is quite obvious that the extraction with alcohol increases the diffusion constant considerably. To prove that this increase is due to the removal of an interfering substance that must be already present in the wool in the raw state, the following experiment was done. Two samples from the solvent-scoured wool were boiled under reflux, one with ether and the other with alcohol, for 3 hrs., and the solvent was evaporated from the samples. The results, given in Table IV, show that the extraction must be at least partly a reversible process.

Other experiments not described here confirm this theory and indicate that the substance in question is sorbed by the wool fibers. This will also explain why none of the scouring methods used is capable of removing this substance from the wool.

### Damage to the Epicuticle

A treatment which is known to impair the epicuticle is to immerse the fiber in alcoholic potash [7]. Two sets of experiments were done in which samples of unextracted and alcohol-extracted tops were treated for different times in a white spirit-butyl alcohol-KOH mixture containing 2.5 g. KOH and 40 ml. butyl alcohol per liter of white spirit. The samples were afterwards neutralized in 0.1$N$ $H_2SO_4$, extracted with ether, and buffered as described above. Table V and Figure 2 give the results. Figure 2 shows the dependence of $D$ on the time of treatment. From this figure and the third column in the table it is seen that the treatment with alcoholic potash has a very marked influence on the diffusion constant which is independent of that brought about by the alcohol extraction. It is suggested that this former influence is due to a change in the epicuticle, and this theory is strongly supported by the curves in Figure 2, where it is

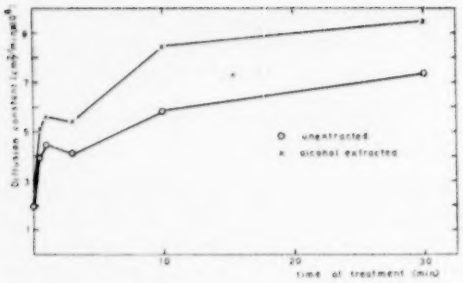


FIG. 2. *Curves showing the diffusion constant of HCl in wool fibers after various times of treatment with alcoholic potash.*

TABLE V

| Time of treatment | Unextracted samples | Alcohol-extracted samples | Difference between alcohol-extracted and unextracted samples |
|---|---|---|---|
| 0 | 1.95 | 2.68 | 0.73 |
| 5 sec. | — | 3.63 | — |
| 30 sec. | 3.93 | 5.08 | 1.15 |
| 1 min. | 4.43 | 5.60 | 1.17 |
| 3 min. | 4.08 | 5.43 | 1.35 |
| 10 min. | 5.83 | 8.48 | 2.65 |
| 30 min. | 7.33 | 9.48 | 2.15 |

The figures are values of $D$ in cm.²/min. $\times 10^6$

seen that an immediate rise in the diffusion constant is brought about by a short treatment. This very rapid increase is best explained by the presence of a thin outer layer which strongly affects the diffusion constant. After that, $D$ increases slowly, probably because the attack of the alkaline agent extends deeper into the fiber. The reason why an undamaged epicuticle will give a lower diffusion constant is obviously that the diffusion constant for the thin layer forming the epicuticle is extremely low. This phenomenon might necessitate a different treatment of the diffusion equation which takes into consideration this inhomogeneity [6].

Several values for other acids and for fibers contaminated by spinning oils, detergents, etc., have been obtained and will be reported later. It will only be mentioned that the differences between the sorption rates of such acids as HCl, $HNO_2$, HBr, and $H_2SO_4$ are very small, $H_3PO_4$ and $H_2C_2O_4$ being more rapidly sorbed.

It is possible to obtain more accurate measurements by using recording devices, and the method is believed to be a good and simple one for evaluating the influence of the epicuticle and the surface properties on the reactivity of the wool fibers.

## Summary

A method for measuring the diffusion rate of mineral acids in wool fibers has been developed. It consists mainly in dispersing short fibers in acid solutions and measuring the decrease in the concentration by means of a conductivity cell. The diffusion constant is obtained by solving the diffusion equation for the conditions specified. The experimental curves agree well with the theoretical ones. In this way the importance of the epicuticle for the diffusion phenomena in wool fibers has been proved. The presence of an undamaged epicuticle gives a low diffusion constant. The necessity of removing all foreign matter which may interfere with the diffusion has been stressed.

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# The Application of *N*-Carboxy Anhydrides of Amino Acids to Wool

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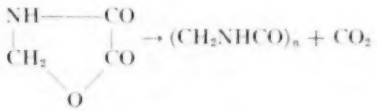
## Introduction

In recent years much interest has been shown in the polymerization potentialities of the *N*-carboxy anhydrides of α-amino acids [3, 7]. Woodward and Schramm have produced polymers of average molecular weights of several million by copolymerization of *N*-carboxy-*L*-leucine anhydride and *N*-carboxy-*DL*-phenylalanine anhydride in benzene [17]. Similar compounds containing long-chain aliphatic groups have been used for making textiles water-repellent by direct polymerization on the fibers. Useful surface-active agents have been prepared by condensation of simple *N*-carboxy anhydrides with long-chain aliphatic amines [5].

Baldwin, Barr, and Speakman [4] polymerized *N*-carboxy-glycine anhydrides *in situ* on wool and found that the surface film of polyglycine so produced greatly decreased the felting shrinkage of woven wool fabric. The reaction proceeds thus in an inert solvent in the presence of water, which acts as a catalyst:



The properties of the polymer which is formed are discussed in the second part of this communication.

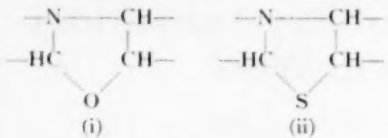
Baldwin, Barr, and Speakman found that the optimum conditions for producing felting-shrinkage resistance by this means were treatment at 50°C for 6 hrs., with 5% of the reagent dissolved in ethyl acetate to which 2% (by volume) of water had been added to initiate polymerization, the liquor-wool ratio being 33:1. Two remarkable features of this process are the small amount of polymer necessary to give almost complete felting shrinkage resistance and the greatly enhanced wear properties of fabric which has received the treatment. Although it was claimed that the process would not change the characteristic properties of the wool in woven fabric, it was noticed that, unless certain precautions were taken, the handle of knitted fabric was seriously impaired. There has been no reference in the literature to the control of felting shrinkage of wool by using *N*-carboxy anhydrides other than that of glycine, and in view of the special merits of the process using this parent compound, we considered it desirable to investigate its homologues, in particular those containing long-chain aliphatic substituents.

Speakman and coworkers have suggested that the film of polyglycine is anchored to the wool fibers by reaction of the polymer with basic side chains on the wool derived from amino acid residues such as arginine and lysine. Detailed investigation of the mechanism of the process has now revealed that the theory of chemical anchoring is untenable, and an account of this aspect of the work forms the subject of Part II of this communication.

Difficulties arise from the high sensitivity of *N*-carboxy-glycine anhydrides to moisture, which would necessitate special precautions in the handling of the material on a large scale. Also, industrial processing of wool fabric in organic solvents introduces many difficulties and the use of an aqueous medium is preferable; hence, attention was directed towards the production of a more stable monomer and, if possible, one that could be applied to wool in an aqueous medium.

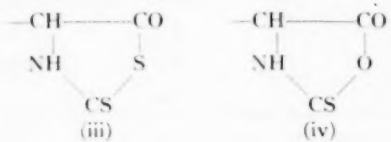
The *N*-carboxy anhydrides of amino acids exhibit few, if any, of the characteristics of heterocycles, their reactions being almost exclusively those of internal anhydrides. The corresponding thiazolidines would be expected to possess more heterocyclic characteristics and the desired stability. As is well known, oxazoles (i) are susceptible to acid hydroly-

sis, whereas the thiazoles (ii) have great stability, being almost insusceptible to attack by hot nitric acid.



(i) (ii)

By virtue of its smaller effective nuclear charge, resulting from an additional electron layer, the sulfur kernel exhibits a smaller inductive effect than does that of oxygen. The reactivity of systems such as R—N=C=O and R—N=C=S (for example, with donor reagents) is governed by the effective nuclear charge of the terminal bivalent atom; increased nuclear charge is accompanied by increased reactivity. Thus, the greater stability of the isothiocyanates as compared with isocyanates is reflected in their slow rates of combination with alcohols and their resistance to attack by water. For these reasons compounds (iii) and (iv) were prepared and their properties examined.



(iii) (iv)

## Part I: Their Use in the Control of Felting Shrinkage

### Experimental Procedure

*Materials*

Unless stated to the contrary the *N*-carboxy anhydrides used in these experiments were prepared by the Bergmann method [6], in which the insoluble carbobenzoxy derivatives are made directly from the amino acid and benzyl chloroformate and are reacted with thionyl chloride or phosphorus pentachloride.

*N-carboxy-glycine anhydride* was prepared with 70% yield based on the glycine and was 97.8% pure, as determined by loss of carbon dioxide.

*N-carboxy*-DL-*alanine anhydride*.—There is no reference in the literature to the optically inactive form of alanine anhydride. After several recrystallizations from ether, the wart-like crystals had m.p. 45–46°C (d).* (Experimentally determined composition: C, 41.6%; H, 4.6%; N, 12.9%. $C_4H_5O_3N$ requires: C, 41.8%; H, 4.4%; N, 12.2%.) Poly-*DL*-alanine formed by the decomposition of a solution of the monomer in dioxan, using water or pyridine as a catalyst, was almost completely soluble in water. Some insoluble polymer was precipitated from a solution of the monomer in diethyl carbonate and decomposed with a pH 8 buffer during 5 hrs. at 50°C. The amino nitrogen content of this material was 1.10%, corresponding to an average molecular weight of 1,270.

*N-carboxy*-DL-*α-aminovaleric anhydride*, prepared via carbobenzoxy-*DL*-aminovaleric acid and recrystallized from chloroform and petroleum ether, had m.p. 66°C. No satisfactory analysis of the compound was obtained owing to its instability.

The polymer was found to be insoluble in all organic solvents and in strong lithium bromide solution.

*N-carboxy-α-aminocapric anhydride*, prepared via *N*-carbomethoxyaminocapric acid and recrystallized from benzene, had m.p. 86–87°C (d). Polyaminocapric acid had a slightly waxy consistency.

*N-carboxy-α-aminolauric anhydride*, prepared via *N*-carbomethoxyaminolauric acid and purified by precipitation from dioxan solution with petroleum ether, had m.p. 90°C. (Experimentally determined composition: C, 65.1%; H, 9.6%; N, 5.8%. $C_{15}H_{23}O_3N$ requires: C, 64.7%; H, 9.5%; N, 5.8%.) This anhydride was considerably more stable than the lower members (compounds derived from amino acids with shorter side chains, such as those derived from glycine or alanine), and the polymer produced from aqueous dioxan had a waxy consistency and when dry exhibited pronounced triboelectric properties.

* "d" stands for "melts with decomposition."

*N-carboxy-α-aminostearic anhydride*, prepared by a method similar to that used for the lauryl homologue, had m.p. 82–83°C and was the most stable of the anhydrides investigated. No visible signs of decomposition were apparent on warming the substance with water, but when it was heated a few degrees above its melting point carbon dioxide was evolved and a waxy solid was obtained.

*N-carboxy-sarcosine anhydride*, prepared via carbobenzoxysarcosine and recrystallized from chloroform, had m.p. 99–100°C. Attempts to produce from this compound a polymer which is insoluble in water were unsuccessful.

*N-carboxy-N-phenylglycine anhydride* was prepared by reaction of phosgene with an aqueous alkaline solution of *N*-phenylglycine according to the method of Fuchs [9]. Recrystallization from benzene gave needles, m.p. 142°C (d). Reaction with water during 30 min. at 75°C produced a low-melting-point gum which was soluble in solvents, which on heating above 100°C *in vacuo* decomposed further, yielding a viscous material capable of being drawn into long filaments.

*3,4-dihydro-dithiazole-5-one* (*iii*), prepared independently by a method similar to that already reported by Cook, Levy, and Heilbron [8], had m.p. 275°C and quickly was discolored on standing in the atmosphere. Aqueous buffer solutions at pH 7 and 9 decomposed the compound on warming to 60–70°C, evolving carbon disulfide and hydrogen sulfide and leaving a dark-brown solution. No insoluble polymer was produced.

*2-thio-5-oxazolidone* (*iv*) was prepared by a method which will be published elsewhere. Recrystallized from chloroform, it had m.p. 108°C (hexagonal plates). Decomposition with an aqueous buffer solution at pH 9 proceeded slowly, with the evolution of carbonyl sulfide and gradual deposition of polyglycine of molecular weight 300–450.

*Wool.* The fabric used throughout the investigation was knitted fabric from 2 ends of 17/1 yarn of 64's quality Merino wool. Samples of from 4 to 5 g. in weight were extracted for 6 hrs. with alcohol, 6 hrs. with ether, and washed in running water overnight. They were then dried to constant weight at 110°C.

### *Measurement of Milling Shrinkage and Weight Changes*

All of the treated wool samples were milled by hand in 0.5% soap solution at 20°C. together with an untreated sample. The area shrinkage was determined by measurement with a ruler. All of the samples were relaxed in soap solution before being milled so as to release all set in the fabric. To determine weight changes on milling the fabric was rinsed in water at 50°C for 30 min., extracted with alcohol for 3½ hrs., and again rinsed in water at 50°C for 30 min. The average weight loss of an untreated sample after this process was 0.9%.

### *Method of Application*

The application of the *N*-carboxy anhydrides was carried out in a glass vessel fitted with a condenser and a sealed stirrer protected with a guard. The wool samples were suspended in the solvent by means of cotton thread and the reaction vessel was kept at constant temperature by being placed in a thermostat. Samples were immersed for 30 min. in different M/5 buffer solutions to each of which one or two drops of a nonionic wetting agent had been added to assist the wetting out and were then rinsed for 10 min. in cold water. The wool was conditioned for most of the experiments to a regain of about 13.5%. The average loss in weight during immersion in a pH 9 buffer for 30 min. was 0.1%, and, although samples were used which had been extracted thoroughly with alcohol and ether, it was found that diethyl carbonate at 50°C extracted an additional 0.2% consisting of fats.

After treatment with the various *N*-carboxy anhydrides, the samples were given a light scour with an anionic compound at pH 9.6 for 10 min. at 50°C, rinsed, and finally dried at 110°C. The untreated wool lost 0.1% of its weight during this scour.

## Results

### *Treatment with N-Carboxy-Glycine Anhydride*

The conditions of application of N-carboxy-glycine anhydride, the material used by Baldwin, Barr, and Speakman [4], were investigated in detail since preliminary experiments established the fact that a number of important points had not been recognized by these workers.

*Effect of the pH of the wool.*—Preliminary experiments using wool samples that had been given various pretreatments established the importance of the pH of the wool to the results of the treatment. Samples were treated with 5% *N*-carboxy-glycine anhydride (on the weight of the wool) in ethyl acetate containing 2% water at 50°C for 5 hrs. at a

ratio of solvent volume to weight of wool of 35 : 1 (Table I).

Maximum substantivity occurred in the case of the pH 9 buffer pretreatment. No further experiments were carried out using an ethyl acetate medium because it was found that the small amount of water necessary for the reaction gave rise to an appreciable quantity of acetic acid resulting from hydrolysis of the ester. A more detailed investigation of the pH effect was therefore carried out using pure diethyl carbonate. The latter was chosen for its low volatility, the low solubility of water in it, and comparative neutrality.

Wool samples conditioned to different pH values and at a regain of 13.5% were treated with 5% *N*-carboxy-glycine anhydride (on the weight of the wool) in diethyl carbonate containing 2% water for 2 hrs. at 50°C at a liquor-wool ratio of 33 : 1.

Table II shows that the small amount of polymer deposited at pH 1.5 was removed completely on milling and the additional loss of 1.2% is slightly more than the average loss in weight of normal wool on milling. The deposit became permanent only when the pH was 5.0, when the milling shrinkage of the treated sample also began to be reduced. Higher pH values resulted in progressively greater permanence of the polymer (*i.e.*, the polymer is not removed so easily on washing and milling). From a practical standpoint, the pH 9 pretreatment seemed to be the most effective, since it resulted in maximum substantivity after milling. No advantage was gained by prolonging the buffer treatment, as is shown in Table III.

Resistance to milling shrinkage was nullified if the excess pH 9 buffer was not rinsed off prior to treatment with *N*-carboxy-glycine anhydride. In one such experiment with wool at regain 16.5%, the milling shrinkage was 33.9%, as compared with a control shrinkage of 33.5%.

TABLE I. EFFECT OF pH OF WOOL ON APPLICATION IN ETHYL ACETATE

| Pretreatment | pH | Milling shrinkage (%) | Control shrinkage (%) | Weight increment (%) | Weight increment after milling (%) |
|---|---|---|---|---|---|
| Tap water | 7.5 | 0.6 | 31.4 | 2.5 | 1.5 |
| Buffer | 5.0 | 20.0 | 29.0 | 2.4 | 1.6 |
| Buffer | 9.0 | 1.3 | 35.6 | 3.0 | 2.5 |
| 2*N*-cyclohexyl-amine | 9.5 | 18.0 | 31.8 | 2.1 | 1.5 |
| 2*N*-$NH_4OH$ | 10.0 | 12.0 | 31.8 | 2.6 | 1.7 |
| Aqueous pyridine | 8.5 | 26.1 | 31.3 | 0.26 | — |

The basicity of the wool was also modified by immersion of a sample dried at 110°C in a 10% solution of pure diethanolamine in absolute alcohol. The excess liquors were removed by squeezing and the volatile solvent was removed *in vacuo* at room temperature, leaving about 10% of diethanolamine distributed throughout the wool. The sample was then treated with 5% *N*-carboxy-glycine anhydride in diethyl carbonate containing 2 cc. of diethanolamine at 50°C for 2 hrs. The solubility of diethanolamine in diethyl carbonate is of the same order as that of water in the same solvent and therefore the decomposition of the anhydride would be expected to follow the pattern of the previous experiments using water. The wool sample showed a loss in weight of 0.4% and the milling shrinkage was 33.2%.

TABLE II. EFFECT OF pH OF WOOL ON APPLICATION IN DIETHYL CARBONATE

| Buffer solution | pH | Milling shrinkage (%) | Control shrinkage (%) | Weight increment (%) | Weight increment after milling (%) |
|---|---|---|---|---|---|
| Dilute HCl | 1.5 | 33.2 | 34.4 | 0.6 | −1.8 |
| Citric phosphate | 2.0 | 36.6 | 30.3 | 1.5 | −0.6 |
| Citric phosphate | 4.0 | 23.0 | 30.5 | 1.2 | −0.6 |
| Citric phosphate | 4.5 | 31.8 | 27.2 | 1.3 | −0.5 |
| Citric phosphate | 5.0 | 26.1 | 27.2 | 1.4 | −0.1 |
| Citric phosphate | 5.5 | 9.5 | 30.1 | 1.3 | — |
| Citric phosphate | 5.8 | 0.2 | 30.3 | 1.4 | +0.7 |
| Citric phosphate | 6.0 | 1.0 | 30.3 | 1.4 | 0.6 |
| Citric phosphate | 6.5 | −0.4 | 30.5 | 1.4 | 0.5 |
| Citric phosphate | 7.0 | 5.9 | 34.4 | 1.6 | 0.5 |
| Citric phosphate | 8.0 | 2.2 | 32.2 | 1.7 | 0.7 |
| Borax phosphate | 9.0 | 1.1 | 32.2 | 1.8 | 1.2 |
| $NH_4OH$-$NH_4Cl$ | 10.0 | 0.0 | 30.4 | 2.2 | 0.8 |

TABLE III. EFFECT OF PROTRACTED pH 9 BUFFER PRETREATMENT

| Time of immersion in pH 9 buffer (hrs.) | Weight increment (%) | Weight increment after milling (%) | Milling shrinkage (%) | Control shrinkage (%) |
|---|---|---|---|---|
| 0.5 | 1.8 | 1.1 | 3.3 | 25.2 |
| 1 | 1.8 | 0.9 | 3.8 | 25.2 |
| 24 | 1.8 | 0.9 | 3.8 | 22.0 |

TABLE IV. EFFECT OF CHANGE IN WATER CONCENTRATION IN DIETHYL CARBONATE

| Vol. of water added to 140 cc. of solvent (cc.) | Milling shrinkage (%) | Control shrinkage (%) | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|---|
| 0.5 | 5.2 | 26.1 | 1.3 | 1.2 |
| 1.0 | 1.4 | 26.1 | 2.2 | 1.6 |
| 1.5 | −2.0 | 26.9 | 2.8 | 2.2 |
| 2.0 | −2.3 | 26.9 | 2.8 | 2.0 |

as compared with a reference-sample shrinkage of 32.6%.

In another experiment, 10% of *N*-carboxy-glycine anhydride was padded onto a dry wool sample from diethyl carbonate. After removal of the solvent *in vacuo*, the sample was treated with anhydrous benzene containing 2 cc. of anhydrous pyridine at 50°C for 3 hrs. at a liquor-wool ratio of 33:1. A weight increase of 0.2% was observed, but the shrinkage resistance was negligible.

*Optimum Conditions of Application.*—In the following experiments, pretreatment in a 0.2*M* buffer at pH 9 was adopted as a standard procedure.

The effect of changing the water content of the bath was studied at a constant temperature of 50°C for 5 hrs. at a liquor-wool ratio of 35:1. Wool samples were treated with 5% *N*-carboxy-glycine anhydride after having been brought to a regain of 13.4% after pretreatment in a buffer at pH 9, as described above. See Table IV.

From Table IV it is seen that the optimum water content is between 1% and 2% by volume.

From a practical point of view it was desirable to reduce the time of treatment of 5 hrs. which was previously used. A high degree of shrinkage resistance was obtainable after 1 hr. at 50°C, but a threefold increase in the weight of polymer deposited was realized after 2 hrs. at the same temperature (Table V).

TABLE V. EFFECT OF TIME OF TREATMENT WITH WOOL OF 13.4% REGAIN AT A LIQUOR-WOOL RATIO OF 35:1

| Time of treatment (hrs.) | Reagent on weight of wool (%) | Milling shrinkage (%) | Control shrinkage (%) | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|---|---|
| 1 | 5 | 2.9 | 34.0 | 0.9 | 0.6 |
| 1½ | 5 | 0.0 | 34.0 | 1.3 | 1.1 |
| 2 | 5 | 3.3 | 32.5 | 2.2 | 2.1 |
| 5 | 5 | −2.0 | 26.9 | 2.8 | 2.2 |

TABLE VI. EFFECT OF TEMPERATURE

| Temperature (°C) | Milling shrinkage (%) | Control shrinkage (%) | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|---|
| 30 | 16.0 | 31.0 | 1.2 | 0.0 |
| 40 | 12.6 | 31.0 | 1.3 | 1.0 |
| 50 | 3.3 | 32.5 | 2.2 | 2.1 |
| 60 | 2.2 | 31.0 | 0.8 | 0.2 |

The optimum temperature for the treatment was found to be 50°C, other factors remaining constant (Table VI).

From Table VII it is seen that the ideal regain for the wool is about 17% and that an effective treatment can be obtained with as little as 3% of reagent (on the weight of the wool) if a 25:1 liquor-to-wool ratio is employed.

TABLE VII. ADJUSTMENT OF REGAIN, CONCENTRATION OF REAGENT, AND LIQUOR-WOOL RATIO

| Regain of wool (%) | Liquor-wool ratio | % Reagent on weight of wool | Milling shrinkage (%) | Control shrinkage (%) | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|---|---|---|
| 13.5 | 35:1 | 5 | 3.3 | 32.5 | 2.2 | 2.1 |
| 13.5 | 35:1 | 4 | 8.0 | 31.2 | 1.4 | 1.3 |
| 13.5 | 35:1 | 3 | 13.1 | 31.2 | 0.6 | 0.4 |
| 11.3 | 35:1 | 5 | 4.4 | 29.4 | 0.8 | 0.1 |
| 15.0 | 35:1 | 5 | 6.8 | 30.1 | 1.4 | 0.6 |
| 16.6 | 35:1 | 5 | 0.7 | 30.1 | 1.7 | 1.4 |
| 17.4 | 25:1 | 3 | 0.0 | 31.0 | 1.2 | — |
| 17.5 | 25:1 | 2 | 10.3 | 39.0 | 0.8 | 0.5 |
| 17.5 | 25:1 | 1 | 31.0 | 39.0 | 0.2 | — |
| 20.0 | 25:1 | 2.5 | 12.6 | 28.0 | 0.8 | −0.7 |
| 23.7 | 25:1 | 2.5 | 16.6 | 28.0 | 0.7 | — |

TABLE VIII. APPLICATION OF A MIXTURE OF *N*-CARBOXY-AMINOCAPRIC AND *N*-CARBOXY-GLYCINE ANHYDRIDES

| Aminocapric derivative (%) * | Glycine derivative (%) * | Conditions of treatment | Milling shrinkage (%) Treated sample | Milling shrinkage (%) Control sample | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|---|---|---|
| — | 5.0 | 6 hrs. at 50°C | 1.3 | 19.0 | 4.1 | 2.0 |
| 10.0 | — | 6 hrs. at 50°C | 14.1 | 23.7 | 4.0 | 0.2 |
| 0.5 | 4.5 | 6 hrs. at 50°C | 1.4 | 19.0 | 4.8 | 1.8 |
| 1.0 | 4.0 | 6 hrs. at 50°C | 2.3 | 22.4 | 2.8 | — |
| 1.5 | 3.5 | 6 hrs. at 50°C | 3.9 | 20.1 | 3.2 | — |
| 1.75 | 3.25 | 6 hrs. at 50°C | 10.0 | 20.1 | 2.8 | — |
| 2.0 | 3.0 | 6 hrs. at 50°C | 24.3 | 20.7 | 4.0 | −0.1 |
| 3.0 | 2.0 | 6 hrs. at 50°C | 21.4 | 20.7 | 4.4 | 0.8 |
| 2.0 | 4.0 | 6 hrs. at 50°C | 17.8 | 24.3 | 4.7 | — |
| 3.0 | 4.0 | 6 hrs. at 50°C | 8.3 | 24.3 | 5.8 | — |
| 4.0 | 4.0 | 6 hrs. at 50°C | 5.7 | 23.3 | 5.3 | 0.6 |
| 10.0 | — | 3 hrs. at 70°C | 32.5 | 34.5 | 2.1 | −0.1 |

* On weight of wool.

TABLE IX. APPLICATION OF OTHER ANHYDRIDES

| *N*-carboxy anhydride | Conc. (on wt. of wool) (%) | Conditions of treatment | Milling shrinkage (%) Treated sample | Milling shrinkage (%) Control sample | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|---|---|---|
| Aminostearic | 8 | 6 hrs. at 50°C | 18.5 | 21.7 | 1.6 | −0.3 |
| Aminostearic | 8 | 5 hrs. at 75°C | 17.5 | 21.6 | 0.2 | — |
| Aminolauric | 13 | 3 hrs. at 60°C | 35.9 | 29.4 | 0.1 | — |
| Aminovaleric † | 10 | 3 hrs. at 50°C | 29.4 | 34.6 | 1.5 | −0.1 |
| *N*-phenylglycine | 20 | 3 hrs. at 70°C | 30.0 | 25.6 | 0.4 | −0.6 |
| Sarcosine | 10 | 3 hrs. at 50°C | 35.5 | 32.8 | 0.6 | −0.8 |

TABLE X. COMPARISON BETWEEN *N*-CARBOXY-GLYCINE AND *N*-CARBOXY-*DL*-ALANINE ANHYDRIDES

| Anhydride | Conc. (on wt. of wool) (%) | Conditions of treatment | Milling shrinkage (%) Treated sample | Milling shrinkage (%) Control sample | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|---|---|---|
| *DL*-alanine | 5 | 3 hrs. at 50°C | 30.6 | 30.7 | 1.2 | −0.1 |
| *DL*-alanine | 7 | 3 hrs. at 50°C | 13.5 | 30.9 | 1.4 | −0.5 |
| Glycine | 5 | 3 hrs. at 50°C | 4.5 | 35.7 | 2.2 | 1.1 |
| Glycine | 7 | 3 hrs. at 50°C | 4.0 | 35.7 | 2.4 | 1.9 |

*Application of Higher N-Carboxy Anhydrides and a Sulfur Analogue*

In general, the conditions of application of the higher anhydrides (containing long hydrocarbon chains) were the same as the optimum conditions described above: at 50°C, 17% regain, and a liquor-to-wool ratio of 25:1. Any deviations from these conditions are specified.

Table VIII shows the results obtained when wool was treated with the aminocapric homologue alone and in admixture with the parent compound.

The normal process using *N*-carboxy-glycine anhydride began to break down for concentrations of reagent of less than 3.5% (on the weight of the wool). In the case of experiments with 4% *N*-carboxy-glycine anhydrids, a certain amount of copolymerization took place on the fibers, as was evident from the slightly tacky handle of the fabric.

The results of application of the aminostearic, aminolauric, aminovaleric, sarcosine, and *N*-phenylglycine anhydrides are shown in Table IX. A comparison of the results obtained with *N*-carboxy-

TABLE XI. APPLICATION OF *N*-CARBOXY ANHYDRIDES OF *N*-PHENYLGLYCINE AND GLYCINE BY PADDING

| *N*-carboxy anhydride | Pretreatment of wool and baking temp. | Milling shrinkage (%) Treated sample | Milling shrinkage (%) Control sample | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|---|---|
| *N*-phenylglycine—20% soln. in diethyl carbonate | pH 10 pretreatment; baked at 100–110°C for 1 hr. | 32.7 | 32.1 | 3.5 | 0.5 |
| *N*-phenylglycine—20% soln. in diethyl carbonate | No pretreatment; baked at 100–110°C for 1 hr. | 34.5 | 32.1 | 4.0 | 0.5 |
| *N*-phenylglycine—20% soln. in diethyl carbonate | No pretreatment; baked at 140–150°C for 1 hr. | 26.6 | 26.5 | 5.4 | 0.2 |
| Glycine—5% solution in diethyl carbonate | No pretreatment; baked at 75°C for 3 hrs. | 21.5 | 30.8 | 0.5 | −0.5 |

glycine and *N*-carboxy-*DL*-alanine anhydrides is shown in Table X.

It was shown that the polymer from the phenylglycine anhydride changed on heating; hence, padding a strong solution of the compound onto the wool from its solvent, using an expression of 100% followed by baking, was tried. No shrinkage reduction was obtained. This method of application was also tried with *N*-carboxy-glycine anhydride, but it failed to give shrinkage reduction (Table XI).

The sulfur analogue, 2-thio-5-oxazolidone, was applied from diethyl carbonate at concentrations of 12.5% and 15% (on the weight of the wool) under the optimum conditions described above (Table XII).

Although a considerable deposit of polymer remained permanent to hand-milling, a reduction in milling shrinkage of only 25% was observed.

TABLE XII. APPLICATION OF 2-THIO-5-OXAZOLIDONE FROM SOLUTION

| Conc. of reagent (%) | Milling shrinkage (%) Treated sample | Milling shrinkage (%) Control sample | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|---|
| 12.5 | 17.4 | 22.7 | 3.9 | 3.1 |
| 15.0 | 17.9 | 22.7 | 4.4 | 3.8 |

## Discussion

The optimum conditions for rendering knitted wool fabric unshrinkable with *N*-carboxy-glycine anhydride were shown to be:

1. An initial pretreatment in a buffer at pH 9.
2. Drying to a regain of approximately 17%.
3. Treatment at 50°C for 2 hrs. with 3% of the reagent dissolved in diethyl carbonate to which 1% by volume of water has been added, the liquor-wool ratio being 25:1.

These conditions for the effective treatment of wool are more economical from a practical point of view than those described in the literature. Whereas wool conditioned at pH 9 offers almost complete felting shrinkage resistance on treatment with 3% of *N*-carboxy-glycine anhydride in diethyl carbonate, the weight of polymer deposited is less than that obtained by Speakman's technique. The handle of the pretreated fabric was much superior. During the course of the investigation it was often noted that some samples of wool treated by Speakman's method possessed a better handle than others. It is possible that this variation is due to an uneven distribution of alkali on the wool and a consequent uneven deposition of polymer. Equilibration with an aqueous buffer solution would render the wool equally basic throughout, ensuring a more even distribution of the polymer.

The only other compound besides *N*-carboxy-glycine anhydride which showed a tendency to reduce the felting shrinkage of wool was the corresponding *N*-carboxy-*DL*-alanine anhydride. The polymers from the higher amino acids showed no substantivity and did not reduce felting shrinkage. The more stable sulfur compound similarly failed to render wool unshrinkable, and *N*-carboxy-glycine anhydride appears to be the only compound of this group which can be used successfully for this purpose.

# Part II: The Nature of the Reaction Between *N*-Carboxy-Glycine Anhydride and Wool

## Polymerization of *N*-Carboxy-Glycine Anhydride

Wessely [16] describes the decomposition products of *N*-carboxy-glycine anhydride under various conditions. Water vapor at room temperature over a period of 2 mo. brought about a 42.0% loss in weight due to evolution of carbon dioxide. Calculated weight loss for the formation of a polymer $(-NHCH_2CO-)_n$ amounts to 43.56%. Dilution of the reagent with water at room temperature greatly reduced the yield of water-insoluble materials and the total amino nitrogen content of the products was increased. Glycine formation was quantitative with normal sodium hydroxide. Wessely [16] reported a sharp drop in the amino nitrogen content of the decomposing solution when normal sodium hydroxide was added over a longer period but could offer no explanation of this phenomenon.

Our observations regarding the influence of pH on the degree of felting-shrinkage resistance imparted to wool and those of Wessely [16] on the aqueous decomposition of *N*-carboxy-glycine anhydride suggested that the nature of the polymer formed may depend on the pH of the solution. This seemed all the more likely, since wool is at its isoelectric zone at pH 4–7 and hence it is difficult to see how the pH effect can be ascribed to changes in the wool.

### *Effect of pH on the Decomposition of N-Carboxy-Glycine Anhydride*

Buffer solutions used were composed as follows: 0.2*M* disodium hydrogen phosphate + 0.1*M* citric acid over the range pH 2-pH 8; 0.1*M* dihydrogen potassium phosphate + 0.05*M* sodium borate at pH 9.

Pure *N*-carboxy-glycine anhydride (1 g.) was dissolved in anhydrous dioxan (10 cc.) and the temperature of the solution was maintained at 30°C in a thermostat. Decomposition was effected by addition of a buffer solution (5 cc.) at 30°C. The approximate times to produce turbidity and for completion of the reaction were noted. At the end of 1 hr. the precipitated polymer was filtered through a Gooch crucible of known weight, washed with cold water, and dried to constant weight at 110°C.

The terminal amino nitrogen of the polymer was estimated, using the standard van Slyke technique. The polymer was dissolved in a few cc. of 100% lithium bromide solution (w./v.)* and decomposed with excess nitrous acid, and the volume of nitrogen liberated was measured accurately.

Table XIII and Figure 1 show the relation between the pH of the reaction and the amino nitrogen of the resulting insoluble polymer.

TABLE XIII. EFFECT OF pH OF REACTION ON AMINO NITROGEN CONTENT OF POLYMER

| pH of solution | % Amino nitrogen of polymer | Weight of polymer (g.) | Average molecular weight | Time to produce turbidity (sec.) | Approx. reaction time (min.) |
|---|---|---|---|---|---|
| 2.2 | 3.50 | 0.60 | 400 | 90 | 45 |
| 4.3 | 2.30 | 0.61 | 610 | 30 | 45 |
| 5.1 | 1.81 | 0.62 | 775 | 30 | 25 |
| 6.1 | 1.88 | 0.50 | 745 | Immediate | 17 |
| 7.1 | 1.80 | 0.50 | 775 | Immediate | 15 |
| 7.9 | 1.70 | 0.52 | 825 | Immediate | 8 |
| 9.0 | 1.57 | 0.40 | 895 | Immediate | 8 |

The rate of decomposition was found to be greatly influenced by pH. The reaction time, which was approximately 45 min. at pH 2.2, dropped steadily with increase of pH, finally remaining stationary at pH values 7.9 and 9.0. The molecular weight of the polymer produced was a function of the reaction rate

* "w./v." stands for the weight for volume—*i.e.*, 100 g. of lithium in 100 cc. of water.

TABLE XIV. ANALYSIS OF POLYMER PRODUCED AT pH 9.0

| | Description of fraction | Weight (g.) | Amino nitrogen (%) | Average molecular weight |
|---|---|---|---|---|
| I | Original polymer | 1.73 | 1.53 | 930 |
| II | Polymer soluble in boiling water | 0.15 | 3.02 | 460 |
| III | Polymer insoluble in boiling water | 1.58 | 1.30 | 1080 |
| IV | Polymer insoluble in 30% lithium bromide (w./v.) | 1.18 + 0.40 | No change | No change |
| V | Polymer insoluble in 65% lithium bromide (w./v.) | 1.11 | 0.68 | 2060 |

and this explains some of Wessely's results [16]. The anomalous experiment in which *N*-NaOH produced higher polypeptides can be interpreted as being the result of a crude buffer action provided by the slow addition of the alkali.

An unbuffered solution of *N*-carboxy-glycine anhydride has an acid reaction and will produce larger amounts of lower polypeptides, which fact is borne out by the following experiment.

*N*-carboxy-glycine anhydride (1 g.) was dissolved in anhydrous dioxan (10 cc.) as above and decomposed at 30°C by the addition of tap water (5 cc.). Polymerization took place slowly and the final pH of the solution was found to be 4.2.

The yield of polymer after washing was 0.51 g. and the amino nitrogen content was 2.7%, corresponding to an average molecular weight of 520.

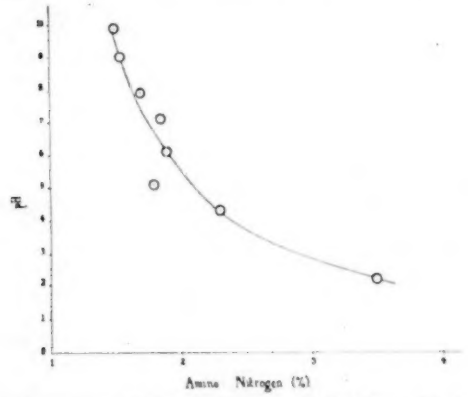



FIG. 1. *Relationship between the pH of the solution of N-carboxy-glycine anhydride and the amino nitrogen content of the resulting polymer.*

TABLE XV. MOLECULAR WEIGHT OF POLYMER OBTAINED AT pH 9

| Average molecular weight | % by weight |
|---|---|
| 2060 | 64.2 |
| >460 <2060 | 27.1 |
| 460 | 8.7 |

*Molecular-Weight Distribution of Polymers Produced at pH 9.0 and pH 4.3*

*N*-carboxy-glycine anhydride (4.00 g.) was dissolved in anhydrous dioxan (40 cc.) and maintained at 30°C in a thermostat. An aqueous pH 9 buffer (20 cc. of 0.05 *M* phosphate-borax) was added at 30°C. After 1 hr. the polymer was collected, dried at 110°C, and weighed (I), boiled with water for 15 min., filtered while hot, and reweighed (III). The hot filtrate was evaporated on the steam bath and the solid residue (II) was weighed. Residue (III) minus an aliquot for end-group determination was digested with 30% lithium bromide solution (24 cc. w./v.) at 95°C for 30 min. The polymer was filtered and washed first with hot 30% lithium bromide solution and then washed repeatedly with hot water. The dried residue (IV) was identical in weight with (III) and no precipitate was formed on dilution of the lithium bromide extract. Residue (IV) was finally digested with 65% lithium bromide (30 cc. w./v.) at 95°C for 30 min. The suspended polymer was filtered and washed with lithium bromide solution and hot water. The final polymer (V) was dried and reweighed. This material dried to a semi-transparent brittle mass. The results of van Slyke amino nitrogen determinations carried out on fractions I, II, III, and V are shown in Table XIV.

Table XV gives the percentage composition of the polymer.

A similar series of extractions of the polymer produced at pH 4.3 gave the analysis and percentage composition shown in Tables XVI and XVII.

The main conclusion to be drawn from these experiments and those demonstrating the influence of pH on the effectiveness of the application of *N*-carboxy-glycine anhydride to wool is that resistance to milling shrinkage is a function of the molecular weight of the polymer deposited on the fibers.

The net charge on the wool changes by very little over the range pH 4 to pH 9, as is illustrated by the very small change in acid-base combining ca-

TABLE XVI. ANALYSIS OF POLYMER PRODUCED AT pH 4.3

| | Description of fraction | Weight (g.) | Amino nitrogen (%) | Average molecular weight |
|---|---|---|---|---|
| I | Original polymer | 1.05 | 2.77 | 505 |
| II | Polymer soluble in boiling water | 0.34 | 4.55 | 308 |
| III | Polymer insoluble in boiling water | 0.71 | 2.56 | 590 |
| IV | Polymer insoluble in 30% and soluble in 65% lithium bromide | 0.58 | 2.16 | 650 |

pacity over this range of pH. Very few more amino groups are available as $-NH_2$ at pH 9 than at pH 4. Wool conditioned on the acid side of the isoelectric point and then placed in fresh water liberates hydrogen ions to the liquid phase; similarly, wool conditioned on the alkaline side of the isoelectric point, even after numerous washings, extracts hydrogen ions from the liquid phase. It is this phenomenon which is responsible for the differences in molecular weight of polyglycine produced inside and on the surface of wool fibers after the latter have received various buffer treatments.

As has already been seen (Table VIII), the waxy polymers produced from anhydrides containing long-chain aliphatic radicals are not firmly held by the wool and hence cannot be expected to produce unshrinkability, quite apart from the fact that in an earlier communication [1] it had been shown that a rigid polymer was required for the prevention of felting. None of the other compounds examined, with the exception of *DL*-alanine derivative, yielded high molecular-weight polymers under the conditions employed, and their failure to render wool non-felting is thus seen to fall into line with the *N*-carboxy-glycine anhydride results, low pH treatments being ineffective because of the low molecular weight of the polyglycine produced.

## Mode of Deposition of the Polymer

### *Extraction of Polymer*

Polyglycine as formed in an aqueous buffer solution at pH 7 is insoluble in cold water, hot organic solvents, and most acids. Boiling water dissolves out the lower polypeptides up to hepta- or octaglycylglycine and reference is made in the literature to their complete solubility in lithium bromide solution and concentrated sulfuric acid [13]. It has now been found that polyglycine is readily soluble in aqueous cupri-ethylenediamine.

TABLE XVII. MOLECULAR WEIGHT OF POLYMER OBTAINED AT pH 4.3

| Average molecular weight | % by weight |
|---|---|
| 650 | 55.2 |
| >308 <650 | 12.5 |
| 308 | 32.3 |

Baldwin *et al.* [4] found that wool fabric that had been treated with *N*-carboxy-glycine anhydride and then extracted with a 50% solution of lithium bromide retained its resistance to shrinkage and their results suggested that the polymer was chemically bound to the wool since a sample of polymer prepared by them was soluble in 50% lithium bromide solution.

During the course of this work it was observed that the purity of the monomer greatly affects the nature of the resulting polymer. An inferior sample of *N*-carboxy-glycine anhydride may give rise to a polymer that is readily soluble in 50% lithium bromide solution at room temperature, whereas polymer derived from a sample that has undergone several recrystallizations and treatment with animal charcoal is insoluble in 50% lithium bromide solution at 50°C. It has already been shown that over 60% of the polymer produced at pH 9 remains insoluble on digestion with 65% lithium bromide solution (w./v.) at 95°C. It is of interest in this connection that specimens of polyglycine have been observed to increase in molecular weight on standing in the air for several months.

Preliminary experiments with cupri-ethylenediamine and 100% lithium bromide solution (w./v.) provided evidence that polyglycine could be extracted from wool treated with *N*-carboxy-glycine anhydride under the optimum conditions.

### *Extraction with Aqueous Cupri-Ethylenediamine [15]*

Cupric hydroxide (6 g.) was dissolved in ethylenediamine hydrate (8.5 g.) and the solution was made up to 100 cc. with water and filtered through a sintered-glass funnel. Polyglycine was readily soluble in this solution on warming. Addition of methanol to the solution precipitated a dark solid which redissolved in water. Acidification of the latter solution reprecipitated the polymer. Wool that had been treated

TABLE XVIII. LITHIUM BROMIDE EXTRACTION OF TREATED SAMPLES

| Sample | Initial weight increase (%) | Weight increase after LiBr extraction (%) | Initial shrinkage (%) | Final shrinkage (%) |
|---|---|---|---|---|
| Treated | 2.0 | −0.1 | 1.4 | 31.3 |
| Control | — | 0 | 27.8 | 37.5 |
| Treated | 2.1 | −0.4 | 0 | 21.7 |
| Control | — | 0 | 25.1 | 28.2 |

with *N*-carboxy-glycine anhydride readily lost its polymer deposit to the solution on warming. However, owing to the high alkalinity of the solution, which degrades the wool, the reagent could not be used to determine quantitatively the amount of polymer removed.

*Extraction with Aqueous Lithium Bromide*

Two 4-g. specimens of knitted wool fabric were immersed in a buffer solution at pH 8 and brought to a regain of 17% in the usual way. They were given a treatment with 5% *N*-carboxy-glycine anhydride in diethyl carbonate for 2 hrs. and then a light scour with an anionic wetting agent was applied. After the weight increment had been determined, the samples were immersed in 80 cc. of 100% (w./v.) aqueous lithium bromide solution for 2 hrs. at 50°C. A second 2-hr. treatment was given with fresh lithium bromide solution at the same temperature. Two controls were run under identical conditions but without *N*-carboxy-glycine anhydride and then immersed in 50 cc. of 100% lithium bromide solution at 50°C for 2 hrs. All four specimens were washed in water at 50°C for 30 min., allowed to stand in running water at room temperature for 2 days, and then dried to constant weight at 110°C. It was apparent from the results shown in Table XVIII that the polyglycine deposit was stripped from the fabric. The treated samples had now regained their felting power. On adding water to the lithium bromide solution the polymer immediately precipitated out as a fine white suspension.

A further experiment was carried out in which the wool was given a prolonged treatment (5 hrs.) with *N*-carboxy-glycine anhydride in ethyl acetate without the buffer pretreatment (Table XIX).

TABLE XIX

| Sample | Weight increase (%) | Weight increase after LiBr extraction (%) | Shrinkage (%) |
|---|---|---|---|
| Treated | 3.2 | 0.3 | 16.6 |
| Untreated | — | −0.1 | 31.3 |

The lithium bromide extract was diluted with water and the precipitate of polymer was collected in a weighed Gooch crucible. The amount of solid obtained after heating to constant weight at 110°C represented 1.7% on the original weight of the wool. Allowing for the loss in weight shown by the control, there still remained 1.3% on the weight of the wool to be accounted for. The most probable explanation is that a considerable quantity of lower polypeptides are formed inside the fibers and held firmly in much the same way as inorganic salts are. The removal of the major part of the high polymer by dissolving in lithium bromide solution liberates these lower polypeptides, which are then capable of remaining dispersed even in very weak solutions of lithium bromide. To confirm the formation of a substantial quantity of lower polypeptides under the application conditions, the following experiment was carried out.

*N*-carboxy-glycine anhydride (4.00 g.) was dissolved in diethyl carbonate (600 cc.) and decomposed by addition of a pH 9 buffer solution (4 cc.), the temperature being maintained at 50°C for 2 hrs. The polymer was collected and on drying at 110°C it weighed 2.67 g. After extraction with water at 50°C and drying, the polymer weighed 0.49 g.

*Deposition of Polymer on Deaminated Wool*

As a further argument in support of the theory that the polymer is held by chemical bonding, Baldwin *et al.* [4] deaminated wool with van Slyke reagent and found that wool thus treated could no longer be rendered unshrinkable with *N*-carboxy-glycine anhydride. They conclude: "There can be little doubt, therefore, that the basic side-chains of wool play a fundamental part in the production of unshrinkability, presumably because they initiate polymerization of the *N*-carboxy-glycine anhydride on the fibers and anchor the polymer thereto."

It has been observed on repetition of this work that, after deamination using the van Slyke reagent and adjusting the pH of the deaminated wool to 9.0, effective treatment is possible with N-carboxy-glycine

TABLE XX. TREATMENT OF DEAMINATED WOOL BROUGHT UP TO A REGAIN OF 17%

| Sample | Milling shrinkage (%) | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|
| Untreated | 20.0 | — | — |
| Treated | 2.6 | 1.8 | 1.2 |
| Deaminated treated | 0.7 | 2.2 | 1.1 |

anhydride under normal conditions of application (Table XX).

Our experiments on the influence of the pH of the wool offer an obvious explanation of the results quoted by Baldwin *et al.* After deamination the wool is in an acid condition which is very difficult to change without an alkaline aftertreatment. It was this acidity, and not the removal of amino groups, which was responsible for the lack of shrinkage resistance.

Since wool deaminated with van Slyke reagent is dark orange-brown in color and obviously undergoes a profound change during the long period of immersion in acid, corroboration of the effect of amino groups was sought by treating wool acetylated by a process used widely in Germany [2]. Wool acetylated to the extent of a 77% decrease in acid-combining capacity and treated with *N*-carboxy-glycine anhydride under the optimum conditions showed a milling shrinkage of 6.4% as compared with 33.5% for a reference sample (Table XXI).

Silk and nylon contain few basic groups. Reaction of the former with *N*-carboxy-glycine anhydride under the optimum conditions and determination of the weight increment after hand-milling revealed a significant substantivity of the polymer (Table XXII).

*Location of Polymer*

A direct visual determination of the location of melamine resin in treated wool fibers has been described by Marshall and Aulabaugh [12]. Small swatches of melamine-treated and untreated wool fabric were refluxed for 1 hr. with a concentrated solution of the dyestuff Aqua Plastic Red and then washed in simmering distilled water until practically no further dye was removed. Examination of cross sections of these fibers under the microscope revealed that the melamine deposits had taken up the stain whereas untreated fibers were practically unstained. These authors claimed that there was a

TABLE XXI. TREATMENT OF ACETYLATED WOOL

| Sample | Milling shrinkage (%) | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|---|
| Acetylated wool | 33.5 | — | −2.0 |
| Normal treated | 2.4 | 1.7 | 1.0 |
| Acetylated treated | 6.4 | 1.0 | −1.7 |

TABLE XXII. TREATMENT OF SILK AND NYLON WITH 5% *N*-CARBOXY-GLYCINE ANHYDRIDE

| Sample | Weight increase (%) | Weight increase after milling (%) |
|---|---|---|
| Silk | 1.8 | 0.4 |
| | 1.7 | 0.6 |
| Nylon | 1.2 | 0.0 |
| | 1.3 | 0.1 |

uniform distribution of the melamine resin within the wool fiber structure.

Application of this differential dyeing technique to fibers treated with *N*-carboxy-glycine anhydride showed that the respective affinities of the dye for fiber polymer were reversed; polyglycine showed very little affinity for the dye. Examination of cross sections of stained fibers showed the treated fibers to be lightly stained, whereas the untreated fibers were heavily stained. There are two possible interpretations of this result: either the polyglycine is located on the surface of the fibers, blocking entry of the dyestuff molecules; or the polymer is very uniformly distributed throughout the fiber structure, masking the sites of dyestuff adsorption of the keratin molecule.

## Reason for Reduction in Felting Shrinkage

It is possible to reduce felting by changing the elastic properties of wool—for example, by introducing new cross-links into the polypeptide chain. Baldwin *et al.* [4] showed from measurements on the work to stretch a fiber 30% that *N*-carboxy-glycine anhydride does not cross-link and this finding was confirmed in this laboratory. The tensile strength of individual fibers was very slightly decreased, whereas an increase in tensile strength would result from cross-linking.

The scaliness of treated fibers in air and in 0.2% soap solution was measured by these authors by

TABLE XXIII

| Sample | $\mu_1$ | $\mu_2$ | D.F.E. $\frac{\mu_1 - \mu_2}{\mu_1 + \mu_2}$ |
|---|---|---|---|
| Untreated | 0.57 | 0.36 | 0.23 |
| Treated | 0.59 | 0.43 | 0.17 |

TABLE XXIV. TENSILE PROPERTIES OF YARN TREATED WITH *N*-CARBOXY-GLYCINE ANHYDRIDE

| | Tested dry | | Tested wet | |
|---|---|---|---|---|
| Yarn treatment | Tensile strength (oz.) | Extension (in.) | Tensile strength (oz.) | Extension (in.) |
| Untreated | 15.2 | 2.4 | 15.3 | 10.2 |
| *N*-carboxy-glycine anhydride at pH 9 | 18.1 | 4.8 | 17.6 | 10.8 |
| *N*-carboxy-glycine anhydride at pH 4 | 14.6 | 3.9 | 16.5 | 10.8 |

means of the lepidometer. Although the scaliness of the treated fibers was 40% less than that of untreated fibers in soap solution, it is impossible to attribute the high degree of felting-shrinkage resistance conferred on wool by *N*-carboxy-glycine anhydride to this cause alone. To investigate the matter further, we decided to compare the result recorded in the literature with scaliness measurements made by two other techniques. Using the "violin-bow" method [10], the differential frictional effect (D.F.E.) for treated fibers in a pH 7 buffer solution was found to be 14% ± 2% compared with 27% ± 1% for the D.F.E. of the control. The second method used was that of Lipson and Howard, which has been applied by Makinson [11] to *N*-carboxy-glycine-anhydride-treated fibers. The D.F.E. was measured by $\frac{\mu_1 - \mu_2}{\mu_1 + \mu_2}$ (where $\mu_1$ is the "anti-scale" and $\mu_2$ the "with-scale" coefficient of friction (Table XXIII)).

These results confirm also the findings of Lindberg and Gralén that the scaliness or D.F.E. is reduced [10] by treatment with this compound, a conclusion which was challenged by Makinson [11]. However, the small reduction in scaliness would not produce the high degree of felting-shrinkage resistance observed in treated samples. Thus, wool given a mild acid chlorination treatment which reduces the D.F.E. by 50% shows hardly any resistance to felting.

Single-fiber measurements having thrown but little light on the mechanism of the anti-shrink effect,

TABLE XXV. WOOL IMPREGNATED WITH POLYISOBUTENE

| Yarn treatment | Weight increase (%) | Dry tensile strength (oz.) | Extension (in.) | No. of revolutions required to wear a hole |
|---|---|---|---|---|
| Control | — | 15.2 | 2.4 | 3,000 |
| 0.2% polyisobutene | 0.2 | 16.7 | 3.1 | 3,040 |
| 1.0% polyisobutene | 1.7 | 18.3 | 3.6 | 3,340 |
| 5.0% polyisobutene | 10.7 | 22.0 | 4.4 | 3,980 |
| 3.0% *N*-carboxy-glycine anhydride | 1.8 | 18.1 | 4.8 | 4,450 |

attention was turned to another aspect of the matter. Wool treated with *N*-carboxy-glycine anhydride has been shown by Baldwin *et al.* to possess remarkable wear-resistance properties. A resistance to wear, as measured by the Toolal-Broadhurst-Lee Ring Wear Tester, of more than three times that of untreated wool has been reported. This may be demonstrated more clearly by plotting the bursting strength of treated woolen fabric against the degree of abrasion. Samples were submitted to a given number of revolutions of the above Ring Wear Tester and the corresponding bursting strength was determined on a Mullen Burst Tester. Figure 2 shows typical curves obtained for wool treated with *N*-carboxy-glycine anhydride under various conditions.

The very slow decrease in bursting strength with increase of abrasion indicated that the yarns comprising the fabric probably possessed a greater tensile strength than untreated yarn. It had been briefly pointed out in the literature that considerable difficulty was experienced in detaching treated yarns and removing individual fibers from untwisted yarn. This local adhesion effect was studied quantitatively by determining yarn tensile strength. The tests were carried out using a Goodbrand Yarn Breaker, which records the extension of yarn at constant rate of load to break. Table XXIV gives figures for 2/18 white yarn treated with 5% *N*-carboxy-glycine anhydride under optimum conditions and for a comparison yarn treated after being conditioned at pH 4.0.

A considerable increase in dry tensile strength was observed with the yarn treated at pH 9.0 but a small decrease in strength was noted in the case of samples pretreated on the acid side, which, of course, showed no shrinkage-resistance. These results show clearly that there is considerable gluing together of fibers in

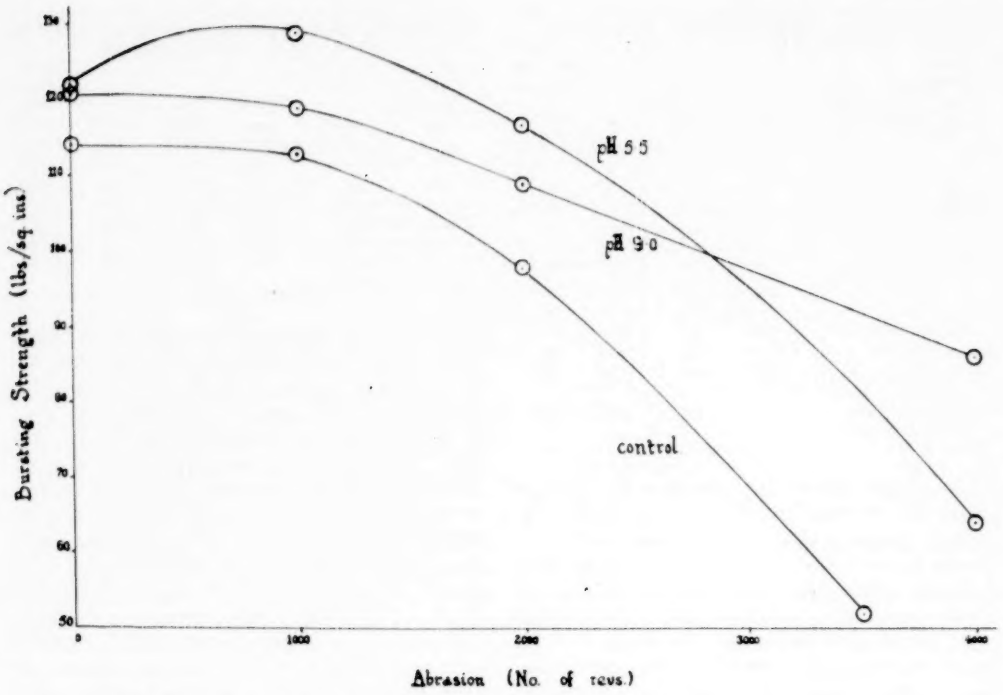



FIG. 2. *Plot of bursting strength against degree of abrasion of woolen fabric treated with N-carboxy-glycine anhydride.*

the yarn since the tensile strength of single fibers is, if anything, lower after treatment than before. Stock and Salley [14] showed that wool yarn treated with melamine resins behaved in an exactly analogous manner (*i.e.*, tensile strength of yarn was increased whereas that of single fibers was unchanged). There is no doubt, therefore, that this gluing effect can lead to shrink-resistance. However, the great increase in abrasion-resistance cannot be explained on this basis alone, as can be seen from the following experiment, in which wool yarn was treated with rubber (polyisobutene) dissolved in chloroform (see Table XXV). Here considerable increase in tensile strength produced only a small increase in abrasion-resistance.

## Conclusions

An explanation of the dependence of milling shrinkage-resistance and the weight increment of polymer upon the pH conditions of the wool is provided by study of the polymerization of *N*-carboxy-glycine anhydride in aqueous buffer solutions. The average molecular weight of the polymer produced is a function of the pH of the solution, being greater at the higher pH. Lithium bromide extraction experiments and the successful application of *N*-carboxy-glycine anhydride to deaminated and acetylated wool have demonstrated unequivocally that the polymer is held on the fibers by physical forces or hydrogen bonding. It is generally accepted that silk owes its rigid structure to hydrogen bonding and it may reasonably be assumed that high-molecular-weight polyglycine is similarly attached to the wool substance. This attachment would be broken down by lithium bromide in the same way that the reagent breaks down silk. The failure of carbon- and nitrogen-substituted *N*-carboxy-glycine anhydrides to render wool unshrinkable can be explained by the inability of the peptide

chains carrying long aliphatic radicals to form hydrogen bonds effectively with wool keratin. In the same way, short polypeptide chains like those in the low-molecular-weight polymers produced under acid conditions would not have the same scope for hydrogen bonding and this explains their failure to prevent felting. The amino groups associated with the lysine and arginine residues in wool exist as the $NH_3^+$ ion at pH conditions below 10–11 pH, and chemical combination with *N*-carboxy-glycine anhydrides would not be expected to take place. The slow combination of hydrogen ions with the keratin in wool conditioned at pH 8–9 is, however, sufficient to provide pH control for the decomposition of the small quantity of anhydride involved.

Examination of fibers treated under optimum conditions has confirmed the observation of Speakman that elasticity plays a very small part in the nonfelting mechanism; it is difficult to interpret scaliness data which have given such widely diverging values for the reduction in D.F.E. as 40%, 50%, and 22%. It is therefore concluded that resistance to milling shrinkage arises from the small reduction in scaliness coupled with local adhesion effects of both fibers and yarns—a feature of the process which contributes to increased wear-resistance and is responsible for the characteristic handle of the fabric.

## Acknowledgment

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# INDUSTRIAL SECTION

## Moisture Determination in Textiles by Electrical Meters: Part IV

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**Abstract**

Previous studies of the precision of various types of electrical moisture meters [8–10] are extended to include meters for sheet materials. The experimental results are analyzed in a manner similar to that previously used and the techniques are extended to cover position and tension effects which could not be covered practically with the bulk materials previously used.

The analysis of precision indicates the following: the instrument which is applicable to continuously moving sheets, such as warps or fabric, has a precision equal to that obtainable from ovens; the instrument in which the sample to be tested is clamped between the electrodes is approximately twice as precise as ovens.

Precautions in the interpretation of these results are indicated.

PREVIOUS PAPERS in this series [8–10] have discussed representative electrical moisture meters for use with bulk textile materials. These publications have presented basic calibration curves for the Hart Moisture Meter, the Moisture Register, and the Steinlite Moisture Tester, and the effects on these curves of temperature variation, presence of dyes or ionizable salts, sample history, etc. Other papers [5–7] have dealt with other aspects of moisture meters and the statistical analysis of test data. This paper completes the study by the Textile Research Institute of representative electrical moisture meters by presenting tests on meters suitable for sheet material.

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### Selection of Instruments

Of the three meters previously discussed, the Steinlite cannot be used for fabrics because of its cell construction; the Moisture Register, although adaptable to fabrics, has a minimum thickness requirement which is not compatible with the samples used for these tests, since it can be met only through the use of multiple layers. The third instrument, the Hart, is most suitable for sheet material and was retained in this study as representative of direct-current resistance meters; two models were used, one for wool and the other for cotton, the two differing only in the series of comparator resistors.

The other meter chosen for test was the Fielden Drimeter, which operates on alternating current of radio frequency and essentially measures dielectric constant; but with this instrument the sample passes between the electrodes without contacting both and

is, therefore, particularly suitable for the moving sheets of material frequently encountered in the textile industry. The Drimeter model used is not only applicable to the wool and cotton included in these studies but is also adaptable to other fabrics. When the instrument is used for wool, it is necessary to double the reading to obtain the moisture value, whereas for cotton the meter is direct-reading. The scale is linear from 0 to 20% .

In use, the Fielden is first standardized against the capacitance of the air between the electrodes. A thoroughly dried fabric sample is then introduced, which alters the capacitance of the circuit and necessitates a second adjustment to a scale reading of "dry." Thereafter, introduction of any sample of the same fabric causes an additional deflection attributable to change of capacitance due to the presence of moisture; the meter registers the moisture content of the sample directly (allowing for any scale factor —*e.g.*, 2.0 for wool, 2.4 for rayon, etc.).

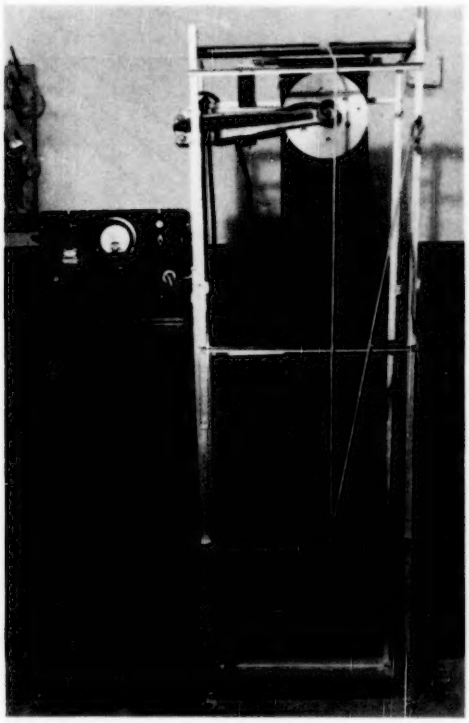

FIG. 1. *Arrangement of Fielden Drimeter equipment for laboratory tests.*

Since the Fielden Drimeter has been designed for sheet material which is in motion, it was necessary to transform the meter into a static instrument for the tests discussed in this paper. Figure 1 illustrates the supporting structure for the electrodes, the meter, and the application of tension to the fabric under test. The plates are placed vertically; in operation, there is no restriction on the position.

## Selection of Materials

Two fabrics were supplied by the Forstmann Woolen Company: (1) a 6.5-oz., lightweight, brown gabardine, 126 by 92; warp, 1/34–1.28; filling, 1/40–R26; (2) an 8-oz. black gabardine with woolen filling, 105 by 55; warp, 1/28–1.26; filling, 5.5-oz. woolen–1.26. These materials will hereafter be designated brown and black gabardine, respectively.

Another wool fabric, obtained from the Prudential Worsted Company, was a 12-oz. multicolor plaid, 48 by 88, woven with 2/40's both ways; in this paper this material will be referred to as plaid.

One cotton sample was unbleached muslin purchased at a local drygoods store. It appeared to be a 5-oz. fabric, 64 by 70; the other cotton sample was a 3-oz. sized cambric, 68 by 68. These materials hereafter will be called muslin and cambric, respectively.

## Preparation of Samples

### *Fielden (Tensioned)*

Samples were prepared from bolt cloth. In all cases, 5 test strips, each 8 in. wide and 54 in. long, were obtained by tearing along the filling. Each strip was turned at the selvage ends and sewed so as to hold rods of various weights when it was desired to provide tension; 5 test areas, 8 in. by 8 in., were marked on each strip, giving an over-all test *pattern* of 5 by 5, 5 positions being along the warp and 5 along the fill (25 in all), as shown in Figure 2. Since the Fielden electrodes were 6 in. in diameter, measured from the inside of the beveled edge, it is unlikely that any measurable portion of the electrical field existed beyond the sample area.

Test strips were hung side by side in a room with conditions controlled to $\pm 1°$F and $\pm 1\%$ relative humidity. Samples were conditioned in positive sorption except for those containing a salt impurity in which desorption was the practice. Unless otherwise specified, samples were conditioned for approximately 1 week.

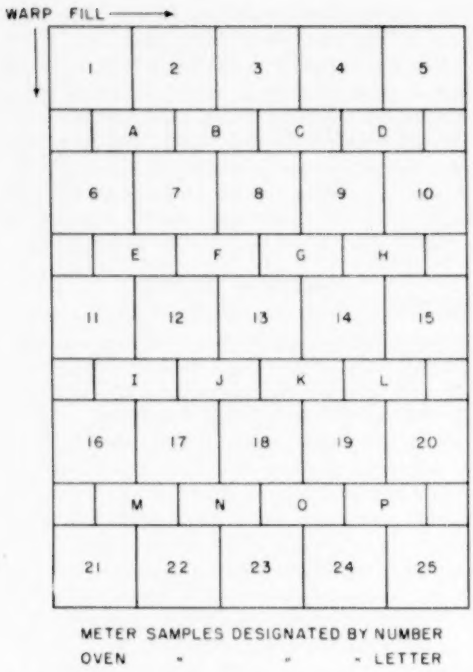


FIG. 2. *Sample pattern for fabric as used in meter and oven tests.*

*Fielden (Untensioned)*

A few tests were made on "untensioned" fabric. While it was possible to use the strips previously described without inserting rods, some of the preliminary tests were made by fastening fabric on a frame similar to a curtain stretcher. All samples referred to in this report as "untensioned" were handled in the latter fashion. The tests on cambric were invariably so conducted; since the material was only 36 in. wide the test pattern was 3 by 8.

*Hart*

The Hart tests were carried out on the samples which had been used for the Fielden. Upon recommendation from the manufacturer, the cotton samples were folded twice (to give four thicknesses) before they were placed between the electrodes; the wool samples, however, were tested in single thickness. In neither case was tension applied. The conditions affecting the Hart calibration curve have been discussed in previous papers [8, 9] and will not be repeated here, except in cases in which the results on fabrics show minor variation from those on bulk samples.

*Oven*

Oven samples were obtained from 4-inch strips torn along the filling. Positions adjacent to those of the instrument test strips were selected. The 16 positions are shown in Figure 2 (labeled *A* through *P*). In the case of the cambric, the oven test pattern was 2 by 7.

## Discussion of Results

*The Fielden Drimeter*

*Tension.*—The Fielden Drimeter measures the moisture of a continuous strip passing between the electrodes. Under textile mill conditions the sample would be under tension; it is, therefore, important to know the effect of this variable on the meter reading.

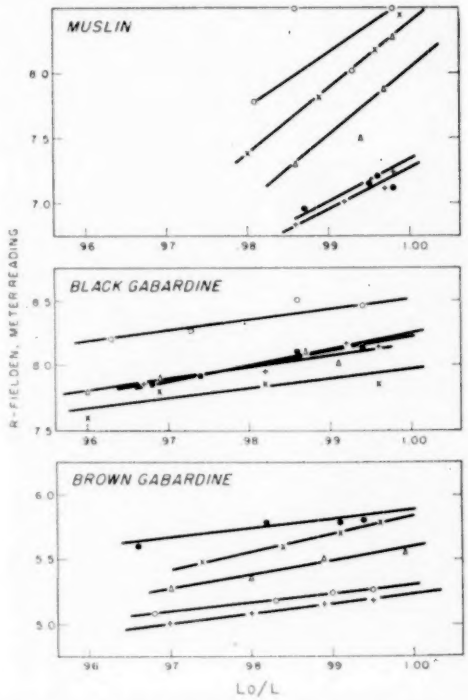


FIG. 3. *Effect of tension on Drimeter readings.*

If tension is applied to a sample of material of length $L_o$, the length is increased to $L$; then the original weight of untensioned material between the electrodes, $W_o$, must be reduced to $(L_o/L)W_o$ if the width of the material does not change. Since capacitance is a direct function of weight of material, a plot of the Fielden reading against $(L_o/L)$ should be a straight line. If $R_o$, the initial reading under no tension, is the same for different samples of the same material, the lines should be parallel. The results verify these hypotheses, although some scattering of points occurs (Figure 3), since accurate measurements of length were difficult to obtain. $R_o$ was not always the same for all samples, so all lines are not parallel.

As a result of these tests, it may be concluded that it is necessary that the Drimeter be set to "dry" with the sample under the tension at which it will be processed, and also that the tension on the strip not be permitted to vary appreciably, since the variation in tension would be incorrectly interpreted as a change in moisture content. Typical effects are illustrated in Table I.

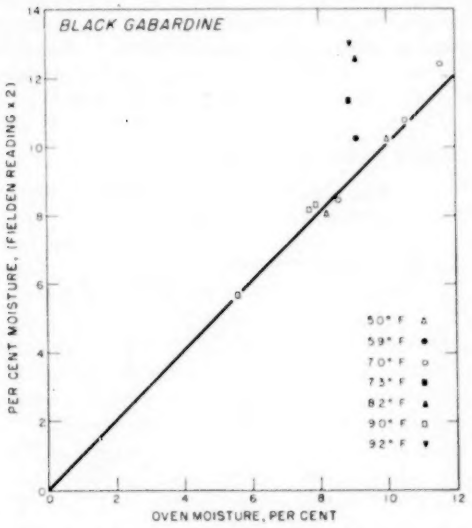


FIG. 4. *Effect of temperature on Drimeter readings. Open symbols indicate that meter was "reset to dry" after each temperature change. Solid symbols indicate that meter was not "reset to dry" after each temperature change.*

TABLE I. VALUES OF Δ READING/Δ TENSION BASED UPON MINIMUM TENSION (¾ LB./FT. WIDTH)

| Material | Tension—lb./ft. width | | |
|---|---|---|---|
| | 1¼ lb. | 3¾ lb. | 7¼ lb. |
| Muslin | −0.192 | −0.137 | −0.099 |
| Brown gabardine | −0.064 | −0.039 | −0.035 |

To anticipate the statistical analysis which will be presented later, a comparison of tests performed on samples under tension with those in which no tension was applied showed that tension increases the variance of a series of measurements, particularly at right angles to the direction of tension, although the variance in the direction of tension is also measurably increased, but to a lesser extent. From the point of view of the mill, this fact is of less importance than it is in static tests, since the electrodes are fixed in one fill position, the cloth is moving continuously, and the meter will therefore tend to average the moisture contents in the direction of tension.

*Temperature.*—The Drimeter is termed "self-calibrating" in the sense that it may be reset to "dry" whenever the type of the material under test changes. Consequently, it is reasonable to assume that the instrument will correctly allow for temperature variation if it is reset when the temperature changes. This assumption is verified by Figure 4. The open symbols represent data on black gabardine taken at a variety of temperatures, the meter being reset at each condition. A single 45° calibration line includes all these data. The solid symbols indicate the effect of temperature when the meter is not reset. Here, the meter was correctly set at the lowest temperature, and the temperature of the room, and therefore of the meter and the sample, was then increased in increments of approximately 10°F. At each temperature level, both Fielden and oven analyses were made on the same sample. The resulting data emphasize the shift in the calibration and the consequent necessity of maintaining a constant temperature if the meter is to read correctly for any single "dry" setting.

It is the belief of the manufacturer, confirmed by actual use [2], that temperature variation between the normal industrial setting and the operating conditions is small. The above remarks on variation of calibration with temperature should, therefore, be considered to be precautionary rather than indicative of a normal error.

*Impurities.*—The presence of impurities in a textile material can affect the reading of electrical meters in two ways. In the first place, they actually alter the moisture regain; if this effect were the only one, the value for moisture content indicated by the meter would be correct even though it would be different from that of the pure fabric. In the second place, if the foreign material should change the electrical properties of the fiber, these properties would affect the meter in the same manner as moisture does; if this effect were the only one, the moisture content indicated by the meter would be higher than the correct one, since the reading would be caused both by moisture and by the impurity. Both of these effects can, and probably do, occur simultaneously.

To check the contribution of electrolyte impurities, some samples were soaked in a 10% NaCl solution and allowed to come to equilibrium from this wet state. The Drimeter was set to "dry" by using a prototype sample which had been thoroughly dried in an oven and stored over Drierite until ready for use. After obtaining a reading of the test sample, the humidity within the conditioned room was increased and at the end of an hour the samples were retested without resetting the "dry" reading. This procedure was repeated until 4 tests were made. With the experiment conducted in this fashion, the salt concentration in the test samples did not vary and all tests were completed without the necessity of resetting the meter. Oven samples were obtained from sections of the strip used for meter analysis to insure reproducibility of salt content.

Figure 5 illustrates the results obtained in these tests, using the black gabardine. It will be noted that large quantities of salt (of the order of 8½%) destroy the linear correlation between the Fielden reading and the oven moisture content. A second similar test was run on an uncontaminated sample of the same gabardine and the results (also shown in Figure 5) were qualitatively the same as before, but the magnitude of the deviations from the expected line was smaller. These small deviations have been attributed to the dye. The brown gabardine (not illustrated) also gave evidence of the possibility of dye effect, although it is doubtful if the deviations measured were significant for this material.

When undyed samples of muslin were treated similarly, the results shown in Figure 6 were obtained. The salted samples show the abnormal effect previously obtained, but the unsalted samples give a straight line that is parallel to the expected calibration line although it lies slightly below it. This displacement is in the correct direction if it is assumed that the "dry" sample gained some moisture as it

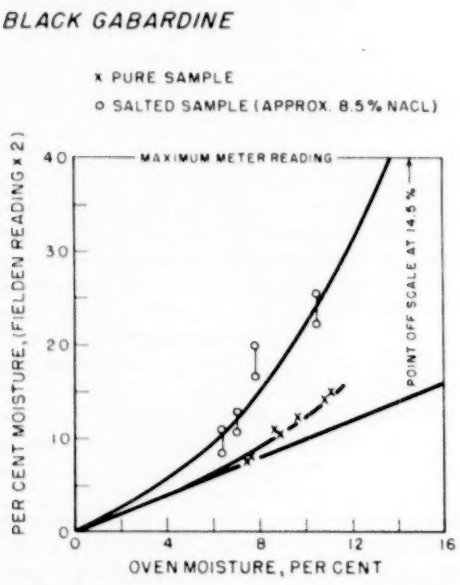


FIG. 5. *Effect of impurities on Drimeter readings.*

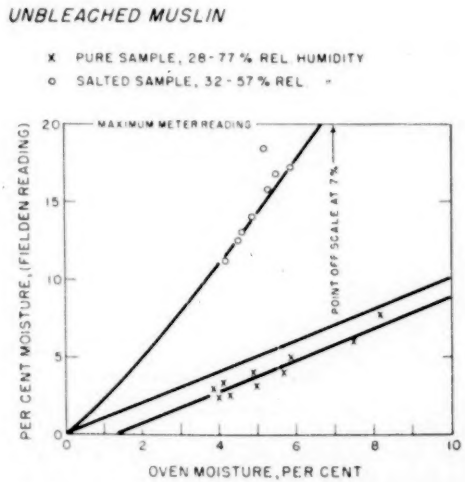


FIG. 6. *Effect of impurities on Drimeter readings.*

was being transferred to the electrodes for the initial setting. In this case, the meter would be "set-to-dry" with a sample containing a small amount of moisture and all subsequent readings at this setting would be low.

The explanation of the abnormalities reported lies in the effect of moisture on the impurities present. As moisture increases, an increasing proportion of the salt may contribute to the electrical properties, and thus the effect of a definite percent of moisture on the meter-reading is greater than that which would be predicted for the pure material. In the absence of foreign matter, or if the foreign matter has no electrical effect, the moisture content indicated by the meter and the true moisture content should be directly related.

It should be emphasized that these laboratory tests represent extreme conditions not likely to be met in the mill. Clutz [2] reported that dyes ranging in pH from 2.7 to 6.7 gave no calibrating difficulty. According to Coles [3], experiments showed that of all the impurities tested sodium chloride caused the greatest abnormalities and that wool samples treated with varying concentrations of sulfuric acid had normal calibration curves. Where a constant amount of impurities is present to such an extent that serious deviations are encountered, special calibrations are required and are entirely possible.

*The Hart Moisture Meter*

The major characteristics of the Hart Moisture Meter have been discussed in earlier papers [8, 9] and will not be repeated here. All Hart readings were reported in terms of an equivalent reading on a single button (*e.g.*, E-button). This procedure indicates that all measurements were taken with an unbalanced circuit. Although this conclusion is untrue, the method does require that a daily record of the relationship of dial readings on different buttons be made in order to be certain that the conversion to the reference button does not change because of voltage drop in the batteries, ageing of the vacuum tube, etc.—precautions which may be easily overlooked. The meter is usually calibrated for a more suitable, null-point-reading method; thus, if the C-button is depressed and the meter shows circuit balance, the moisture content is, say, 6.2% by previous calibration; the null point with the D-button might be 6.8, with the E-button, 7.4, etc. This discontinuous scale is not suitable for statistical treatment of data, but it can be made continuous by the following simple treatment.

Assign numbers 1 to 10 to the buttons A to M, respectively; take readings of the dial scale with contact made through resistor buttons which most nearly approximate circuit balance; interpolate to express this result in terms of the numerical scale assigned to the letters. As an example, suppose that the following readings had been obtained:

$$D = -2.4\ ^{*};\ E = +4.2.$$

The converted Hart reading would then be

$$4.0 + \frac{(+2.4)}{(+2.4) + (4.2)} = 4.36.$$

Because of the change to this system of converting the Hart instrument data to a continuous scale, it was decided to make calculations comparing the old method to the new. The variances, tabulated in Table IV, indicate that the precisions estimated by the two methods are essentially equivalent. Since the new method is more logical and a more acceptable representation of the actual operation of the Hart instrument, it has been used throughout all of the work reported in this paper and is recommended in preference to that published previously [8, 9].

## Conclusions

*Fielden*

Under normal mill operation, the Fielden Drimeter is a self-calibrating moisture meter when set to "dry." Its standard deviation, as indicated by the majority of these laboratory tests, is about ± 0.14% moisture, which compares favorably with the figure of ± 0.12% for the oven. When subjected to abnormal temperature variation, the presence of certain impurities, or variations in tension, the calibration is affected, but it may be noted that these variations should not occur in normal mill operation.

*Hart*

The standard deviation for the Hart Moisture Meter has been determined as ± 0.07% moisture, compared to ± 0.12% for the oven. The meter is, therefore, approximately twice as precise as the oven.

* A minus sign indicates that the needle registers a reading to the left of the dial zero.

TABLE II. ANALYSIS OF VARIANCE, BROWN GABARDINE; WARP, FILL, MOISTURE, AND TENSION AS VARIABLES

| | | Mean square | d.f. | Components | $\sigma^2$ |
|---|---|---|---|---|---|
| 1 | $W$ | 8.0124 | 4 | $\sigma_E^2 + 4\sigma_{WFM}^2 + 5\sigma_{WMT}^2 + 12\sigma_{WF}^2 + 60\sigma_W^2$ | 0.1136 |
| 2 | $F$ | 0.9988 | 4 | $\sigma_E^2 + 4\sigma_{WFM}^2 + 20\sigma_{FM}^2 + 12\sigma_{WF}^2 + 60\sigma_F^2$ | 0.0076 |
| 3 | $M$ | 346.5016 | 2 | $\sigma_E^2 + 5\sigma_{WMT}^2 + 25\sigma_{MT}^2 + 100\sigma_M^2$ | 3.4640 |
| 4 | $T$ | 4.8448 | 3 | $\sigma_E^2 + 5\sigma_{WMT}^2 + 25\sigma_{MT}^2 + 75\sigma_T^2$ | 0.0632 |
| 5 | $WF$ | 0.5120 | 16 | $\sigma_E^2 + 4\sigma_{WFM}^2 + 12\sigma_{WF}^2$ | 0.0400 |
| 6 | $MT$ | 0.1012 | 6 | $\sigma_E^2 + 5\sigma_{WMT}^2 + 25\sigma_{MT}^2$ | 0.0028 |
| 7 | $FM$ | 0.0764 | 8 | $\sigma_E^2 + 4\sigma_{WFM}^2 + 20\sigma_{FM}^2$ | 0.0024 |
| 8 | $WM$ | 0.7132 | 8 | $\sigma_E^2 + 4\sigma_{WFM}^2 + 5\sigma_{WM}^2$ | 0.1368 |
| 9 | $WFM$ | 0.0300 | 32 | $\sigma_E^2 + 4\sigma_{WFM}^2$ | 0.0048 |
| 10 | $WMT$ | 0.0320 | 24 | $\sigma_E^2 + 5\sigma_{WMT}^2$ | 0.0044 |
| 11 | $WFMT$ | 0.0104 | 192 | $\sigma_E^2$ | 0.0104 |
| | | | 299 | | |

Snedecor tests

9 and 10 vs. 11; $P < 1\%$

5, 7, and 8 vs. 9; $P < 0.1\%$, $<5\%$, and $<0.1\%$, respectively

6 vs. 10; $P < 5\%$

4 vs. 6; $P < 0.1\%$

3 vs. 6; $P < 0.1\%$

2/1 Cannot be rigorously tested for significance, main effects, $\sigma_E^2$ and $\sigma_W^2$. Unimportant in view of size and intended use.

For both of the meters and for the oven, the values for the calculated variances depend upon the experiment conducted, the precautions observed, and the materials used.

## Appendix

### *Application of Analysis of Variance*

In all cases, analysis of variance has been performed with two, three, or four variables, the data studied being: (*a*) the readings taken from the meters multiplied by a scale factor where necessary; or (*b*) the oven moistures as calculated from the oven tests previously described [8]. In the case of the Hart data, it was necessary to transform the discontinuous meter readings represented by a letter on each resistance button into a continuous function of moisture content; this procedure has been described in another section of this paper; the results compare satisfactorily with the system previously used and reported, as also noted.

When only two variables are considered (positions across the warp and positions across the fill), all other variables such as the moisture in, temperature of, and tension on the sample are constant. For a three-factor study, one more of these specific variables may be included. Similarly, in a four-factor study, all but one may be included. In the two-factor analysis, the mean square of each of the two variables alone and of their interaction may be determined. Since there is no means of breaking down the interaction, it is frequently considered to be "error" and is so used here. In the three-factor analysis, the same interaction which is considered to be error in the two-factor analysis can now be determined, and the multiple interaction of all three variables will become the residue and will be designated error. This procedure can be projected to the four-factor analysis as well.

With the exception of error, any mean square calculated in the analysis is composed of a series of contributions. For the calculation of the variance due to one variable, the component contributions must be evaluated and all of the factors, both main effects and interactions, which are significant and which contain this variable must be summed to determine the general effect. For example, in Table II, which shows the results of all the calculations on the brown gabardine at various moisture contents and various tensions, with readings at a variety of positions across and down the warp, the variance for repeated readings in a warp-wise direction may be calculated by summing the individual components of variance for the item marked $W$, plus those for any other designated as $W$-times-another-factor. Thus, for variance due to warp effects, begin at the bottom of the table with 0.0104 for error, add 0.0044 for the warp-moisture-tension effect, 0.0048 for the warp-fill-moisture interaction, 0.1368 for the warp-moisture interaction, 0.0400 for the warp-fill interaction, and 0.1136 for the warp main effect, and 0.3100 will be the total warp variance.

TABLE III. CALCULATED VALUES OF 2-SIGMA *

| Material | Testing tension (lb.) | Fielden | | | | | | Oven |
|---|---|---|---|---|---|---|---|---|
| | | Along warp | Along fill | Individuals | Tension | Along warp | Along fill | |
| Brown gabardine | ½ | 0.84 | 0.44 | 0.23 | | | | |
| | 1 | 0.87 | 0.51 | 0.28 | | | | |
| | 2½ | 0.96 | 0.66 | 0.20 | | | | |
| | 5 | 0.96 | 0.57 | 0.20 | | | | |
| | Combined | | | 0.20 | 0.56 | 1.12 | 0.34 | 0.30 |
| Black gabardine | ½ | 1.08 | 0.49 | 0.20 | | | | 0.20 |
| | 0 | 0.36 | 0.48 | 0.29 | | | | 0.20 |
| Plaid | 0 | 0.48 | 0.51 | 0.34 | | | | 0.20 |
| Muslin | ½ | 1.10 | 0.56 | 0.41 | | | | 0.30 |
| Muslin, separate samples | ½ | 0.92 | 0.62 | 0.50 | | | | 0.12 |
| Cambric | 0 | 1.82 | 1.97 | 1.82 | | | | 0.30 |

* Instrument set for average of preliminary oven moistures, correcting for meter constant, except for plaid and cambric; in these, set to "dry" with separate sample.

Cambric contained size; oven samples showed appreciable positional effects.

When such items have been summed and the square root has been taken, the standard deviation for this effect as tested ($\sigma_W = 0.56$) will be obtained. The standard deviation may be used to establish a "precision" value. The establishment of the limits for such a value customarily involves the introduction of a $t$-value. If the number of samples is reasonably large (*e.g.*, above 10), and the chances of containing a value in the precision range specified is desired to be 19 in 20 (5% level), it may be assumed that this $t$-valve is nearly 2, and the limits then correspond to the normal 2-sigma limits. All values reported in this paper have been made on the assumption that the 2-sigma limit is satisfactory.

Significant interactions, as noted in the preceding remarks, are indicative of the fact that the variables being considered do not have a unique effect, independent of effects from other variables. Frequently, information as to the reasons for these interactions at specific levels of operation may be determined by a breakdown of the table into a series of sub-tables [1]. In no case has such a breakdown in this particular experiment been found to produce any results which had not been determined in other tests.

In all cases, values of the calculated variances depend upon the experiment. It is thought that the instrument precisions may be considered to be general, and that the significant variances attributable to other effects and interactions are correct in direction although dependent in magnitude upon the method of test.

*Results*

*Fielden.*—In Table III the following features exhibited by the 2-sigma limits should be noted. In the case of either type of gabardine, limits for, and therefore the precision of, the Fielden meter and the oven are in the same range. Precision is poorer when tension is not applied than when tension is applied. On the other hand, the introduction of tension means a decrease in precision due to increase of directional variances, the predominant variance increase resulting from effects at right angles to the direction of application of tension.

The majority of the precision tests favor the instrument, with 2-sigma values of 0.20 for the instrument and 0.30 for the oven, as obtained with the brown gabardine. Whereas this evidence is not conclusive proof that the instrument is significantly better than the oven,* it should be reasonably conclusive proof that the reverse is not true. Cambric samples are extremely interesting, showing an immensely high 2-sigma limit (low precision) for the Fielden and a normal value for the oven. The oven

* Since, in this type of test, the higher variance is compared to the lower, the test is one-sided and the usual probability levels, as read from the tables, must be doubled. However, if the results of the various independent tests are pooled, a significant difference would appear to exist.

samples, however, had significant warp- and fill-wise effects which, if included, would raise the limits for oven samples to ± 0.95 and ± 0.78 along warp and fill, respectively, although the oven would retain a significant advantage for this material. The high general variability is thought to be due to the presence of size in the sample.

It is interesting to note that, while the error variances for cotton samples tend to run higher than those for wool, this result was predicted by Fielden [4]. He points out that the large hysteresis loop for cotton is responsible and that this condition is much more apparent in laboratory tests, where the direction of approach to equilibrium is not entirely controllable, than in drying in the plant, where the direction of approach is fixed and definite.

In the case of the brown gabardine, a Bartlett test was applied to the error variances for the same samples under different tensions, but no significant effect could be determined. The same is true of influence of temperature and moisture on error variances. It seems reasonable, therefore, to quote the error variances here reported for the materials studied in absolute terms.

TABLE IV. COMPARISON OF VARIANCES FROM OLD AND NEW METHODS FOR HART CALCULATIONS: BLACK GABARDINE

| | Instrument | | | Oven | | |
|---|---|---|---|---|---|---|
| | $(WF)_I/\beta^2$ | | | $V_o$ | | |
| | Old | New | $V_I/\beta^2$ | Old | New | $(WF)_o$ |
| | 0.0067 | 0.0115 | 0.0094 | 0.0149 | 0.0119 | 0.0087 |
| | 0.0021 | 0.0026 | 0.0029 | 0.0226 | 0.0225 | 0.0282 |
| | 0.0038 | 0.0033 | 0.0031 | 0.0097 | 0.0097 | 0.0063 |
| Pooled | 0.0044 | 0.0058 | 0.0051 | 0.0147 | 0.0157 | 0.0144 |

*Hart.*—Tables IV and V show the comparison of precision of the meter readings by old and new methods and their relation to oven precision. The columns to be compared are $(WF)_o$ and $(WF)_I/\beta^2$.

$(WF)$ terms are the residual interaction variances which may be used as an estimate of error in exactly the same manner as the highest-order interaction for the Fielden. The subscript $I$ refers to data from the Hart instrument, while the subscript $o$ refers to that from the oven.

In Table IV, $(WF)_I$ values must be divided by $\beta^2$ (the square of the slope of the calibration line) to

TABLE V. HART DATA—NEW METHOD

| Material | 1 $V_o$ | 2 $(WF)_o$ | 1 ÷ 2 | 3 $V_I/\beta^2$ | 4 $(WF)_I/\beta^2$ | 3 ÷ 4 | 1 ÷ 3 † | 1 ÷ 4 † | 2 ÷ 4 † |
|---|---|---|---|---|---|---|---|---|---|
| Black gabardine | 0.0119 | 0.0087 | 1.37 | 0.0094 | 0.0115 | 0.82 | 1.27 | 1.03 | 0.76 |
| | 0.0225 | 0.0282 | 0.80 | 0.0029 | 0.0026 | 1.54 | 7.76 | 8.65 | 10.85* |
| | 0.0097 | 0.0063 | 1.54 | 0.0031 | 0.0033 | 0.61 | 4.85 | 2.94 | 1.91 |
| Pooled | | | 1.02 | | | 0.88 | 2.88 | 2.53 | 2.48* |
| Muslin | 0.0013 | 0.0015 | 0.87 | 0.0298 | 0.0092 | 3.24 | 0.04 | 0.14 | 0.16 |
| Muslin | 0.0053 | 0.0038 | 1.39 | 0.0016 | 0.0009 | 1.78 | 3.31 | 5.89 | 4.22** |
| Muslin | 0.0049 | 0.0047 | 1.04 | 0.0016 | 0.0004 | 4.00 | 3.06 | 12.25 | 11.75** |
| Pooled | | | 1.15 | | | 3.01 | 2.14 | 6.09 | |
| Muslin | | 0.0093 | | | 0.0002 | | | | 46.50** |
| Muslin | | 0.0108 | | | 0.0019 | | | | 5.68** |
| Muslin | | 0.0182 | | | 0.0009 | | | | 20.22** |
| Muslin | | 0.0151 | | | 0.0014 | | | | 10.79** |
| Pooled (all muslin) | | 0.0091 | | | 0.0021 | | | | 14.19** |
| Brown gabardine | | 0.0207 | | | 0.0061 | | | | |
| | | 0.0078 | | | 0.0066 | | | | 1.18 |
| | | 0.0247 | | | 0.0071 | | | | 3.48* |
| | | 0.0324 | | | 0.0047 | | | | 6.89* |
| Pooled | | 0.0214 | | | 0.0061 | | | | 3.49* |

Brown gabardine: $\bar{X}_I \pm 0.15$; $\bar{X}_o \pm 0.29$ $\beta = 1.0$
Black gabardine: $\bar{X}_I \pm 0.15$; $\bar{X}_o \pm 0.41$ $\beta = 1.0$
Muslin: $\bar{X}_I \pm 0.13$; $\bar{X}_o \pm 0.19$ $\beta = 1.36$

† Numbers greater than 1.0 indicate an instrument precision greater than that for ovens.
* Significant at 5% level.
** Significant at 1% level.

provide values in units of percent moisture if comparison is to be made with the oven variances.

All variances, when expressed in proper units, for both instruments and oven should have the same value if the precisions are equal. A higher variance would indicate poorer precision.

From a study of Table V, the characteristics of the Hart meter when applied to sheet materials can be readily appreciated. In part of this table results obtained by separation of variance [5] and by the calculation of the interaction as a separate estimate of error are reported. In each case the ratio of oven to instrument variances obtained by the two methods is indicated. It will be noted that the separation-of-variance technique does not in either case remove as much of the total variance as does analysis of variance; the latter has therefore been adopted here; it is to be noted that there are no significant warp-wise and fill-wise effects such as those described for the Fielden tests, presumably because tension was not employed when testing the Hart meter.

To compare the precision of the two methods the interaction for ovens can be divided by the interaction for the instrument. In a predominant number of the tests, this division will yield a value which is significant.* The lower value of variance from the Hart meter indicates a precision more favorable than that obtainable from the ovens, in a ratio of approximately 3 to 1 (1.7 to 1 in terms of standard deviation).

The above remarks are qualified in the same manner as those made concerning this instrument in the previous publications—that is, they apply to analysis, or calibration, of a single uniform material. The calibration is dependent upon type of material, history, temperature, and impurities and is not a unique function for the instrument.

* See footnote, page 407.

**Acknowledgment**

The authors acknowledge with sincere appreciation the efforts of Professor John Tukey of the Princeton University Mathematics Department for advice concerning the experimental design, the kindness of the Fielden Electronics Inc. and Hart-Moisture-Meters in lending instruments for tests, and the generosity of Forstmann Woolen Company and Prudential Worsted Company in supplying cloth samples.

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# Testing Textiles on the Elmendorf Tear Tester

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**Abstract**

Preliminary work has indicated that the tearing characteristics of textile fabrics depend on the speed with which the sample is torn. To obtain quantitative information on this speed dependency, the tear-resistance of a variety of fabrics is being studied over a wide range of tearing speeds, from 0.05 in. per min. to impact at 10,000 in. per min. This range encompasses conventional laboratory test speeds and estimated end-use speeds of tear. The Elmendorf tear tester involves speeds which, while greater than those of conventional tear testers, do not approach the high speeds involved in service. This research was undertaken to determine the magnitude of and variations in the speeds of tear obtained with the use of the Elmendorf machine. The work represents only a portion of a broad research on the mechanism of tear, sponsored by the Chemicals and Plastics Section, Research and Development Branch, Office of The Quartermaster General, which has released this paper on the Elmendorf tester for publication.

## Tearing Speed of Elmendorf Tester

### *A. Equation for Velocity of Jaw Separation*

The Elmendorf tester consists of a pendulum which is inclined to the vertical in the rest position where a sample is mounted in the jaws. Upon release from the rest position, the pendulum swings downward, tearing the sample. The upward swing on the other side of the vertical is measured by a pointer, and the difference in heights of the upward swing with and without a sample is a direct measure of the energy required to tear the sample. A complete description of the instrument and its use is given by the A.S.T.M. Standard Designation D-689 [1]. An analysis of the relations between tear energy and calibration of the scale is given by Carson and Snyder [2].

The simple laws of conservation of energy pertaining to pendulums may be used to calculate the velocity at any point of the swing, before, during, and after the tear.

Two assumptions concerning the mechanism of failure of a hypothetical sample are necessary:

Assumption 1: There is no extension of the tails formed by the tear; that is, at all points the jaw separation equals the initial jaw separation plus twice the length of fabric torn.

Assumption 2: The energy of the pendulum is converted to tear energy uniformly in direct proportion to the change in jaw separation during the time in which the sample is being torn; that is, the energy removed per unit length of tear is constant throughout the tear.

These assumptions will be discussed later. As will be seen, the assumptions of no tail extension and linear tear energy removal are merely convenient for postulating the simplest general case. If these functions are known to be different from the assumed ones, they can, nevertheless, be handled in the same manner and the changes in the final equation will be obvious.

The following equation gives the tearing velocity at any point of jaw separation. (The derivation of this equation is given in the Appendix.)

$$v^2 = 8[\pi r \cos(\varphi - 2)/T]^2 \times \left[\cos\theta - \cos A - \frac{r}{D} f(B) \sin(\alpha/2)\right],$$

where $v$ = velocity of jaw separation, in in. per sec.;
$r$ = distance between top of jaws to center of rotation, in in.;
$\varphi = A - \theta$;

* Present Address: Johnson & Johnson, Chicago, Illinois.

$A$ = angle of pendulum from vertical at rest;
$\theta$ = angle of center of gravity to vertical at any point of jaw separation;
$D$ = length of sample torn, or $2D$ = jaw movement to tear sample;

$$f(B) = [\cos(B - C) - \cos A] - [\cos(B_0 - C) - \cos A]\frac{A + B - C}{A + B_0 - C};$$

$B$, $C$, and $B_0$ are defined in Figure 5;
$\alpha$ = angle of jaw travel after tear begins;
$T$ = period of pendulum swing, sec.

### B. *Evaluation of Terms in Velocity Equation*

The following values were used for the terms in the velocity equation:

Angle $A$ = 70°22′;
Angle $B_0$ = 69°52′;
Angle $C$ = 0°46′;
$D$ = 4.3 cm.;
$r$ = 10.32 cm.;
$T$ = 0.93 sec.;

$f(B)$ and $B$ for each scale reading are given in Table I.

All of the above terms except $r$ and $T$ were taken directly from Carson and Snyder [2]. Both $r$ and $T$ were measured on the instrument in use at Fabric Research Laboratories, $r$ by measurement with a ruler and $T$ by timing a large number of small amplitude swings of the pendulum. A check on the angles as measured by the chord radius method gave:

Angle $A$ = 70°28′;
Angle $B_0$ = 70°28′;
Angle $C$ = 0°53′.

This was considered an excellent check on Angles $A$ and $C$ and a sufficiently close check on $B_0$ to use the tabulated values given by Carson and Snyder. The difficulties mentioned by these authors were encountered here—namely, the uncertainty of the exact center of swing, precision in reading of the scale, and the length of radii involved. Furthermore, the 0°36′ difference observed in $B_0$ would make only a very negligible difference in $v$, as can be seen from the velocity equation.

The velocity equation was used to calculate the velocities of jaw separation given in Table II and Figure 1 for each scale reading by 10's from 0–100. For the last three positions of jaw separation (beyond scale readings of 100) the sample was no longer tearing and $\alpha$ was not increased beyond 49°46′. The time to tear a sample 1.69 in. long with any particular scale reading is shown in Figure 2. This figure was constructed from the areas under the curves obtained by plotting the reciprocal of the ordinates of the curves of Figure 1.

TABLE I. RELATION BETWEEN SCALE READING AND ANGLE $B$

| Scale reading | $B$* | $f(B)$† |
|---|---|---|
| 0 | 69°52′ | 0 |
| 10 | 66°23′ | 0.0566 |
| 20 | 62°37′ | 0.1161 |
| 30 | 58°40′ | 0.1763 |
| 40 | 54°39′ | 0.2349 |
| 50 | 50°28′ | 0.2929 |
| 60 | 45°51′ | 0.3528 |
| 70 | 40°59′ | 0.4113 |
| 80 | 35°28′ | 0.4705 |
| 90 | 29°4′ | 0.5297 |
| 100 | 21°11′ | 0.5876 |

* $B$ for any scale reading is given by Carson and Snyder [2].

† $f(B) = \cos[B - (0°46')] - 0.33600 - (0.02074)\frac{69°36' + B}{139°28'}$.

### C. *Experimental Check of Tearing Speeds*

A rough check on the speed of the Elmendorf tear tester was accomplished by means of the apparatus shown in Figure 3. An electrocardiograph recorder, the "Viso-Cardiette," made by the Sanborn Co., Cambridge, Mass., was used to record the angular position *vs.* time for the Elmendorf pendulum. A sprocket was mounted on the shaft of the Elmendorf sector and the chain around this sprocket turned another sprocket on the shaft of a suitable linear potentiometer. Thus a voltage was applied to the cardiograph which was proportional to the angular position of the sector. A chart speed of 2 in. per sec. was used for recording the swing. This speed was checked by a 60-cycle line signal and found to be quite accurate. The chart was so calibrated that full-scale displacement was twice the angle $A$—that is, the recorder pen was at one-half of full scale with the pendulum vertical, and at zero with the pendulum in the rest position.

The slope of the curve was read and calculated in terms of jaw velocity.

$$S = d\varphi/dt,$$

where $S$ = slope of displacement *vs.* time curve.

From equation (6) in the Appendix:

$$v = r \cos(\varphi/2) d\varphi/dt.$$

Two sets of data were taken: one swing with no sample, and one with a sample of nylon poncho fabric which gave a scale reading of 38.5. The data are given in Table III and the points are plotted in Figure 2. The greatest deviations are under 20%, the average being about 10% or less. This is due mostly to inaccuracy in determining the slope of the cardiograph curve. Since the object of these brief tests was to check order of magnitude, no further experimental work was done.

### *D. Discussion of Assumptions*

Assumption 1 (no extension of tails) is true for paper, but very definitely does not apply to fabrics, especially those fabrics containing yarns of high extensibility. It has also been shown [3] that the extension of the tails in the tongue tear test is related to the crimp in the set of yarns in the tails which hold the load. Since the Elmendorf tester performs a tongue tear it is very likely that tail extensions occur in it also, the only difference being the rate of loading. The effects of rate of tear are being studied, but as yet no data are available on the tail extension occurring at speeds comparable to those of the Elmendorf tester. Once the tail extension is known, its effect on the velocity of jaw separation in the Elmendorf can be taken into account by proper adjustment of the angle $\alpha$.

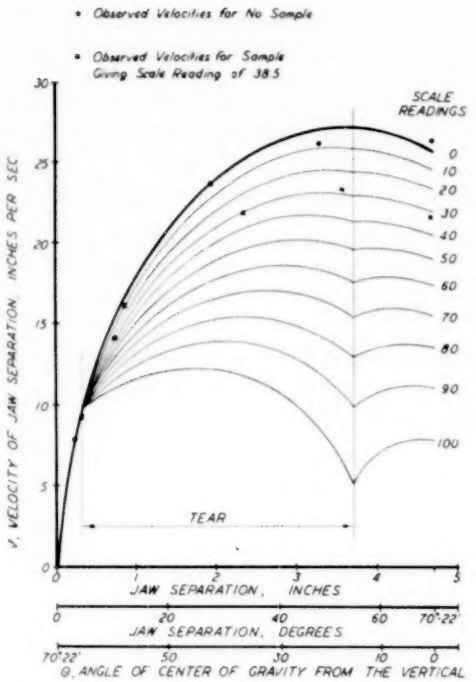


FIG. 1. *Velocity of jaw separation* vs. *jaw separation for various scale readings.*

TABLE II. ELMENDORF TEAR TESTER: VELOCITY OF JAW SEPARATION (IN./SEC.) AT VARIOUS JAW SEPARATIONS FOR EACH SCALE READING *

| Scale reading | JS = 0.31 in.<br>$\theta$ = 65°58′<br>$\alpha$ = 0° | 1.15 in.<br>54°2′<br>11°56′ | 1.98 in.<br>42°6′<br>23°52′ | 2.79 in.<br>30°8′<br>35°50′ | 3.70 in.<br>16°12′<br>49°46′ | 4.00 in.<br>11°22′<br>*a* | 4.30 in.<br>6°28′<br>*a* | 4.68 in.<br>0°<br>*a* |
|---|---|---|---|---|---|---|---|---|
| 0 | 9.7 | 18.9 | 23.8 | 26.3 | 27.2 | 27.0 | 26.6 | 25.7 |
| 10 | 9.7 | 18.4 | 22.9 | 25.3 | 25.8 | 25.7 | 25.4 | 24.5 |
| 20 | 9.7 | 17.8 | 21.9 | 24.0 | 24.4 | 24.4 | 24.0 | 23.3 |
| 30 | 9.7 | 17.1 | 20.9 | 22.7 | 22.9 | 22.9 | 22.6 | 21.9 |
| 40 | 9.7 | 16.5 | 20.0 | 21.5 | 21.3 | 21.3 | 21.1 | 20.5 |
| 50 | 9.7 | 15.8 | 18.9 | 20.1 | 19.6 | 19.7 | 19.6 | 19.0 |
| 60 | 9.7 | 15.1 | 17.7 | 18.6 | 17.5 | 17.8 | 17.8 | 17.3 |
| 70 | 9.7 | 14.4 | 16.5 | 17.0 | 15.4 | 15.8 | 15.9 | 15.5 |
| 80 | 9.7 | 13.6 | 15.2 | 15.2 | 12.9 | 13.5 | 13.7 | 13.5 |
| 90 | 9.7 | 12.8 | 13.9 | 13.1 | 9.8 | 10.7 | 11.1 | 11.0 |
| 100 | 9.7 | 11.9 | 12.2 | 10.7 | 5.1 | 6.9 | 7.7 | 7.8 |

* JS = jaw separation. $\theta$ = angle of center of gravity from vertical. $\alpha$ = angular travel of pulling jaw after tear has commenced. *a* = no more tear energy removed at these positions, taken as 49°46′ for these last three positions.

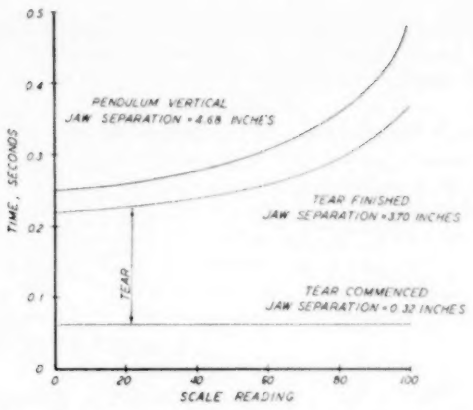


FIG. 2. *Tearing time* vs. *scale reading for samples at various scale readings (length of tear = 1.69 inches).*

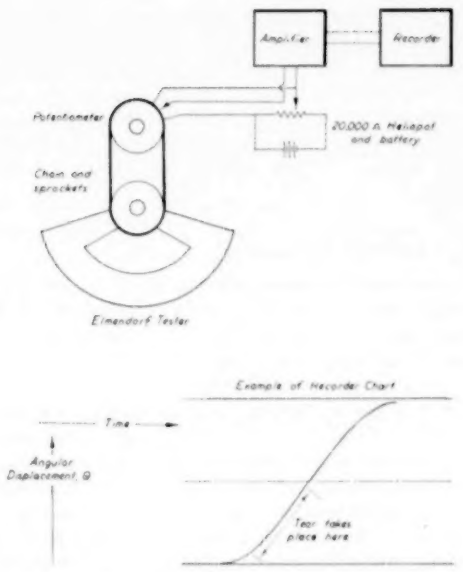


FIG. 3. *Diagram of apparatus for checking speed of Elmendorf tester.*

Assumption 2 (linear rate of tear energy) is also not true for fabrics, since it is well known that a typical load-elongation diagram for tearing fabrics has a saw-tooth shape. Thus the load builds up to a peak value and then drops suddenly (but not to zero) as a yarn or group of yarns is broken. In addition to this situation in the middle of a tear, the load-elongation (and hence energy *vs.* jaw separation) relationship at the beginning of a tear where the sample is being distorted (sometime referred to as "del" formation) is different from that at the end of the tear where a few yarns usually pull out at lower than tear loads, depending upon the tightness of the weave and the smoothness of the yarns. The energy consumed in del formation is quite small as compared to the total tear energy of the 1.69-in. length of sample torn in the Elmendorf. The yarns pulling out at the end in loose fabrics may be of sufficient number to cause a reduction in the 1.69-in length of sample torn. Since it can usually be assumed (especially for light nylon twills, etc.) that only a negligible load is required to pull out these last yarns, the sample can be cut a little longer than the 1.69 in. by an amount corresponding to the number of yarns pulling out.

TABLE III. ELMENDORF TEAR TESTER: EXPERIMENTAL JAW-SPEED DATA

| Without sample: Scale reading = 0 | | With sample: Scale reading = 38.5 | |
|---|---|---|---|
| $\theta$ | JS velocity (in./sec.) | $\theta$ | JS velocity (in./sec.) |
| 66°44′ | 7.7 | 64°58′ | 8.8 |
| 57°11′ | 13.6 | 57°12′ | 16.9 |
| 45°22′ | 22.7 | 40°32′ | 21.7 |
| 23°6′ | 21.6 | 19°14′ | 23.9 |
| 0° | 26.8 | 0° | 21.9 |

In reasonably tight-weave fabrics the errors caused by using Assumption 2 are not large, and tests have shown a good linearity of scale reading with length of sample torn (from about 0.8 to 1.69 in.) on a 60 × 56, 4.7-oz.-per-sq.-yd. cotton sheeting.

It is interesting to note that the pendulum-swing curve obtained with a coated nylon fabric of rip-stop construction did not show any jogs or deviations in the displacement curve, as might have been expected. This is the same coated fabric referred to as "GRS coated Nylon" for which the low speed (3 in. per min.) tongue-tear diagram was given in Figure 10 of reference [3]. In these diagrams the peak load at the rip-stops was over twice the general level of the tearing load. The spacing of these peaks was such that only three of them would occur in the Elmendorf sample. Even though the load probably rose to higher peaks at the rip-stops, the entire swing was a smooth line, as shown in Figure 3. This is not to be regarded as conclusive, however,

since the chain linkage, although quite tight, may not have passed very slight hesitations of the pendulum. However, the precision was good enough to show a twofold change in speed, and the rip-stop peaks were found to be twice the breaking load of the other peaks in the slow-speed test. It is hoped that later work will provide more data on this point.

### *E. Expression of Results*

Of interest at this point is the nomenclature ordinarily used for the Elmendorf tear values. The tear "force" obtained by multiplying the scale reading by 32 (when using augmenting weight) is actually a tear energy, g.-cm./cm., or energy per unit length of jaw separation, since the energy is divided by $2D$ to obtain the "force." However, this term is based on the assumption that 1.0 cm. of jaw separation equals 0.5 cm. of fabric torn. Actually, there is usually tail extension, so that the jaw separation is a fraction more than twice the length of fabric torn. Furthermore, the force so calculated is not the average of the maximum loads (top peaks of the saw-tooth diagram) nor of the lower loads, but somewhere in between, and hence is not the load necessary to tear the fabric, since a higher value of load must be reached to get beyond the first peak. The force so calculated is an "energy-average" one, similar to that recommended by Krook and Fox [4]. However, the energy itself is more useful in comparing the tear-resistance of various fabrics. Such a measure has the added advantage of avoiding any assumptions concerning tail extension or jaw separation, neither of which is determinable by the Elmendorf tester. Thus the energy required to tear a 1-in. length of fabric, *measured before tearing*, may be readily calculated by multiplying the scale reading (using augmenting weight) by $32 \times \frac{2}{454} = 0.141$.

Values thus obtained on cotton fabrics both coated and uncoated, similar to those mentioned above, agree very well with energy values obtained by actually planimetering the area under an autographic diagram obtained by slow-speed tearing on an Instron tester. However, the values for certain coated nylon fabrics did not check at all against those obtained by planimetering, and the difference is believed to have been partially due to differences in test speeds.

TABLE IV. CALIBRATING THE ELMENDORF TESTER WITH ADDED LEAD SECTOR FOR TEARING 16 SHEETS OF BROWN WRAPPING PAPER

| | Scale readings | |
|---|---|---|
| | With lead sector | Without lead sector |
| | 32 | 62 |
| | 30 | 59 |
| | 30 | 59 |
| | 31 | 64 |
| | 31 | 62 |
| | 31 | 62 |
| | 30 | 62 |
| | 31 | 61 |
| | 31 | 64 |
| | 32 | 60 |
| Average | 30.9 | 61.5 |

$\therefore$ Scale ratio $= \frac{61.5}{30.9} = 1.99$. Error $= 0.5\%$.

### *F. Increasing the Capacity of the Tester*

As mentioned previously, the Elmendorf tear tester was primarily designed for testing paper; hence its capacity was comparatively low when it was used for testing fabrics. Even with the augmenting weight, the maximum tear energy which the tester would absorb was 14 in.-lbs. per in. of fabric torn, at a scale reading of 100. The manufacturer does not recommend the use of this tester for scale readings of 80 or more, and this limitation further limits the range of fabrics which may be torn on this machine—for example, the uncoated nylon twill poncho base fabric at about 12 in.-lbs.

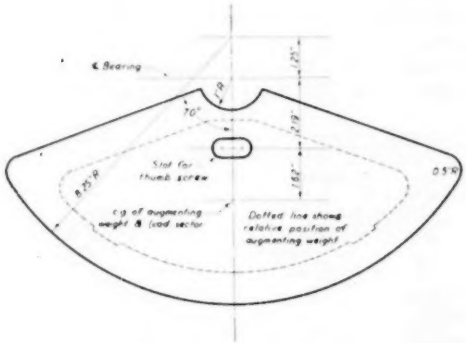


FIG. 4. *Shape of lead sector. Casting to be 0.5 in. thick and weigh 5,000 grams.*

per in. would have a scale reading of about 90. Difficulty arose when attempts were made to tear this fabric. Its behavior was erratic; at times it tore and at other times it did not.

As a means of correcting this difficulty, an additional weight, in the form of a lead casting similar in shape to the original sector and with a weight equal to the weight of the sector plus the augmenting weight, was added. The resulting capacity was exactly twice that obtained with the augmenting weight. The maximum tear energy which the tester would absorb has thus been increased to 28 in.-lbs. per in. of fabric.

To utilize the existing calibrated scale on the machine, a multiplying factor of 2 must be applied to all scale readings obtained with the added lead weight. This was checked by experiments in which samples of brown wrapping paper were tested both with and without the lead weights. The results are given in Table IV. The wrapping paper was used because paper has a more homogeneous construction than textile materials and gives more nearly reproducible results.

The additional weight was so distributed as to give no change in the period of the pendulum swing, and hence no change in the velocity. When using the additional weight it is necessary to clamp the base of the tester to a solid table with large "C" clamps. A pattern of the lead casting is given in Figure 4. The lead weight is fastened to the regular augmenting weight by means of two screws.

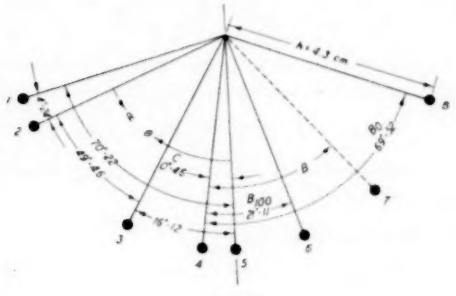


FIG. 5. *Diagram of swing of center of gravity of the Elmendorf tear tester.*

| Position No. | Action Occurring |
|---|---|
| *1* | *Rest, sample mounted in jaws* |
| *2* | *Tear commences, slack due to slit taken up* |
| *3* | *Tear finished (assuming no extension of tails)* |
| *4* | *Zero of scale stops here with no sample in tester* |
| *5* | *Vertical, center of gravity at rest here when not swinging, at highest velocity when free swinging* |
| *6* | *Center of gravity stops here when scale reading = 100* |
| *7* | *Center of gravity stops here when scale reading = X* |
| *8* | *Center of gravity stops here when scale reading = 0* |

## *Appendix*

### Derivation of Velocity Equation

For a pendulum or other falling object, a drop in vertical height transforms potential energy into kinetic energy, which causes acceleration of the mass of the pendulum. If any resistance is encountered to the free fall of the mass, the work done on the resistance diminishes the kinetic energy available to accelerate the mass. Thus:

$$\Delta \text{P.E.} = \text{K.E.} + \text{T.E.}, \qquad (1)$$

where $\Delta$P.E. = change in potential energy; K.E. = kinetic energy available for acceleration of the pendulum mass; T.E. = tear energy to rupture sample.

These terms may be evaluated quantitatively for the Elmendorf tester by means of Figure 5.

The angles $A$, $B$, and $C$ are those given by Carson and Snyder [2], which are shown in Figure 5. The angle at which tear commences was calculated on the assumption of a $\frac{5}{32}$-in. slit in the sample, permitting a jaw separation (chord length) of $\frac{5}{16}$ in. before application of the load. The angle at which the tear was finished was based on a length of sample torn of 1.69 in. [1], permitting a jaw separation of $(\frac{5}{16} + 2 \times 1.69) = 3.699$ in. (see Assumption 1 in text).

From Figure 5 it can be seen that:

$$\Delta \text{ P.E.} = mgh(\cos\theta - \cos A), \qquad (2)$$

where $m$ = mass of the pendulum; $g$ = acceleration of gravity; $h$ = radius to the center of gravity; $\theta$ = angle of center of gravity to vertical; $A$ = initial angle at rest point.

The kinetic energy term for the pendulum is given by:

$$\text{K.E.} = (1/2)I\omega^2 = (1/2)mgh(T/2\pi)^2\omega^2, \quad (3)$$

where $I$ = moment of inertia = $mgh(T/2\pi)^2$; $\omega$ = angular velocity = $d\theta/dt$; $T$ = period of the pendulum swing.

Actually, the velocity of interest is the jaw-separation velocity, $v$, which is the rate of change of the chord length between the jaws:

$$v = dl/dt. \quad (4)$$

The general relation between chord $l$, radius $r$, and central angle $\varphi$ is shown in Figure 6:

$$\sin(\varphi/2) = l/2r. \quad (5)$$

Substituting equation (5) in equation (4),

$$v = 2rd(\sin\varphi/2)/dt = r\cos(\varphi/2)d\varphi/dt = r\cos(\varphi/2)\omega. \quad (6)$$

Substituting equation (6) in equation (3):

$$\text{K.E.} = (1/2)mgh(T/2\pi)^2[v/r\cos(\varphi/2)]^2, \quad (7)$$

where $\varphi = (70°22') - \theta$.

The energy to tear the fabric has been assumed (Assumption 2 in text) to be directly proportional to the length of sample torn, which is equal to the jaw-separation chord length after tear begins. Thus, by the chord-radius method similar to that used in Figure 6:

$$\text{T.E.} = 2rP\sin(\alpha/2), \quad (8)$$

where $r$ = radius to edge of jaw; $P$ = tearing force; $\alpha$ = angle of jaw travel after tear begins.

The tearing force has been derived by Carson and Snyder [2], and is also evident from Figure 5 as:

$$P = (mgh/2D)\left\{[\cos(B-C) - \cos A] - [\cos(B_0 - C) - \cos A]\frac{A+B-C}{A+B_0-C}\right\}, \quad (9)$$

where $D$ = length of sample torn, or $2D$ = jaw movement to tear sample; $\cos(B-C) - \cos A$ = drop in height due to energy removed by tearing of sample; $[\cos(B_0 - C) - \cos A]\frac{A+B-C}{A+B_0-C}$ = drop in height due to energy removed by friction.

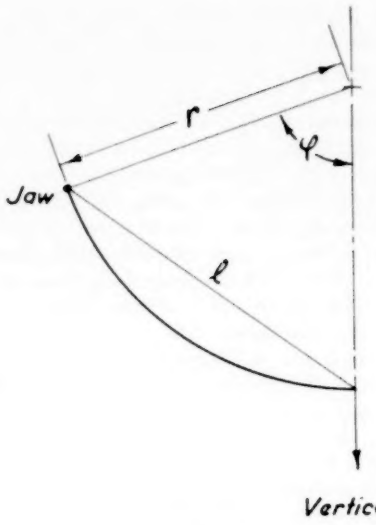


FIG. 6.

Letting $f(B)$ stand for the term in brackets of equation (9), and substituting for $P$ in equation (8):

$$\text{T.E.} = (mgh)(r/D)f(B)\sin(\alpha/2). \quad (10)$$

Substituting equations (2), (7), and (10) into equation (1) and simplifying:

$$v^2 = 8[\pi r\cos(\varphi/2)/T]^2 \times \left[\cos\theta - \cos A - \frac{r}{D}f(B)\sin(\alpha/2)\right]. \quad (11)$$

It should be pointed out that although the tear energy is corrected for friction, equation (11) contains no correction in the velocity for the small amount of kinetic energy consumed by friction. This frictional energy is only a fractional part of the term $(1 - \cos C)$, which is a little less than 0.0001. Thus the velocity correction for friction energy is less than 0.01% and is therefore neglected entirely.

## Summary

The Elmendorf tear tester was originally designed for testing paper but can be used for textiles as well, providing expression of results is altered slightly to take into account stretching of the "tails" of the sample torn. Tearing speeds of the tester have been derived from the mechanics of pendulum motion and checked experimentally with a high-speed

recorder. The maximum capacity was doubled in the same manner as that given by Carson and Snyder to give quadruple the original capacity.

**Acknowledgment**

The work reported in this paper constituted part of a research program on coated fabrics carried out for the Chemicals and Plastics Section, Research and Development Branch, Office of The Quartermaster General.

Gratitude is expressed to Dr. M. M. Platt for suggestions and assistance in calculations.

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# Measurement of Fineness of Cotton by Air-Flow Methods*

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**Abstract**

Using 7 varieties of cotton harvested at different times to give an extremely wide range in fiber development, a study was made of the air-flow method of measuring fineness and maturity of the lint. The data show that when porosity meters are calibrated in units of weight per unit length of fiber (i.e., fineness) the curves for different varieties of cotton are quite different. This is due to the fact that resistance to air-flow through a fiber plug correlates more closely with the surface area of the fibers composing the plug than with their fineness. This surface area varies with variety and maturity, independently of the fineness of the cotton.

Using a plug of constant weight and volume made of fibers having a constant density enables the use of a simple theory which predicts essentially the actual variation of air-flow with both variety and maturity of the cottons tested. Two quite different types of air-flow apparatus are shown to give similar results that are more consistent with the specific surface † of the several cottons than with the fineness of the fibers. For several cottons, the air-flow data published by the U. S. Department of Agriculture for the 1948 crop are compared with the previous 10-year averages for fineness which had been measured by counting and weighing the fibers.

THE ACCEPTED METHOD of determining the "fineness" of cotton is to divide the weight of a counted number of fibers by the product of the number of fibers and their mean length to obtain the average weight per unit length of the individual cotton hairs. Sorting and counting fibers is such a tedious, time-consuming process there has recently been much interest in the use of air-flow through a cotton plug to replace the usual method of measuring fineness. Several workers have devised different methods of applying the general principle, all of which depend upon the resistance to the flow of air through a mass of cotton which is somewhat compressed.

Fowler and Hertel [2] in 1940 showed that air-flow could be used to measure the ratio of the surface area to the mass of fibers in the plug or wad. The method seemed practical on several different kinds of fiber. Since then, Hertel [3] has used a fiber plug in one arm of a pneumatic "Wheatstone bridge" to determine the specific surface of the material.

Pfeiffenberger [5] has used a low rate of flow through a low-density plug. Air is drawn through the plug at a fixed pressure for all cottons and the pressure across a standard orifice in series with the plug indicates the rate of flow through the cotton. The pressures are measured by means of oil manometers, and the readings for cottons of known fineness have been used to establish a calibration curve from which fineness is read from instrument readings for unknown cottons.

Elting and Barnes [1] have devised an apparatus which uses a much denser plug and a higher rate of flow. The pressure drop across an orifice in series with the plug is read on a dial pressure gage. The readings are presented as an "F" factor of the cottons. Elting and Barnes do not believe the instrument will measure fineness uniquely for all cottons of all maturities.

Recently an apparatus called the Micronaire,* which uses a fairly high plug density, has been placed on the market. By means of reducing valves, air pressure is stabilized at a fixed level and the rate of flow of air through the plug is measured by a visible flowmeter of the rotameter type. The scale

* This paper was presented at the meeting of the Fiber Society, Clemson, S. C., April, 1949.

† In this paper, the term "specific surface" is used to mean surface area per unit mass of fiber.

* The Sheffield Corporation, Dayton, Ohio.

on the instrument is graduated in micrograms per inch.

In the opinion of the authors of this paper, all of these instruments are excellent, practical devices, giving valid, reproducible results. It is believed that all of them measure the same thing—namely, the specific surface of the cotton. If the instruments were calibrated in units of specific surface, all would give essentially the same reading for a given cotton. If all of the investigators wanted the reading in terms of specific surface, use of the air-flow methods would be desirable.

When it comes to measuring fineness, the porosity measurements do not seem to agree so well. Consider a thin-walled, coarse-haired cotton, having the same weight per inch as a thicker-walled, fine-haired variety. Since the two have the same weight per inch, there will be the same total length of fiber in the test plug. But, because the surface areas of the samples are so different, it cannot be expected that they will give the same reading in the air-flow apparatus.

The purpose of this study was to determine, theoretically and practically, how well fineness and/or maturity can be measured by air-flow methods.

## Theory

The general problem of air-flow through porous media is quite complex, but, fortunately, the air-flow method applied to measuring fineness is a much simplified form of the general case. This is true for the following reasons:

1. The volume of the plug is constant.
2. The mass of fiber in the plug is constant.
3. The density of all cottons is very nearly constant.
4. From reasons 1, 2, and 3 it follows that the channel space around the fibers in the plug is constant.

Under these conditions it seems that variations in air-flow resistance may be determined almost solely by the surface area of the fibers in the plug.

It has been pointed out that in a pure variety all of the cotton fibers, during growth, have approximately the same diameter. This means that even after shrinkage in drying all fibers of one variety have nearly the same perimeters and, therefore, nearly the same surface area per unit length. This uniformity of fiber perimeter within a variety has been specially mentioned by Pearson [4].

With the assumption that all fibers in a given variety have the same perimeter, rather simple relationships can be shown to exist between air-flow resistance and fineness, and between air-flow resistance and maturity. The derivations are as follows:

### I. Perimeter (Variety) Constant

If $P$ represents the constant perimeter, the area per unit length of fiber is then

$$a = P \times \text{unity} = P.$$

In plugs of fixed weight $W$, the total length of fiber is

$$L = \frac{W}{d},$$

where $d$ is the average weight per unit length of fiber.

The total surface area of the fibers in the plug is then

$$A = La = \frac{W}{d} P.$$

By the assumption that the resistance to air-flow is proportional to total surface area of the fibers in the plug, the rate of flow is

$$R = C \frac{1}{A} = \frac{Cd}{WP},$$

where $C$ is a proportionality constant.

Since $W$ and $P$ are constant, the rate of air-flow is directly proportional to $d$ (*i.e.*, the fineness of the fibers) and when plotted to linear scales should give straight lines, as shown in Figure 1. The two straight lines represent varieties having fine and coarse fibers.

### II. Maturity Constant

When the percent maturity is constant, the wall thickness for all fibers, regardless of variety, will average the same proportion of fiber radii. (The fibers are round during the growing period.) Then, neglecting the weight of the primary wall and assuming the cellulose of the secondary wall to have the same density in all varieties, the perimeters of the fibers will be proportional to the square root of the cross-sectional area of the walls and hence to the square root of their weight per unit length. (This follows from the geometrical principle that any linear dimension of similar geometrical figures is proportional to the square root of the areas.)

So the area per unit length of fiber is

$$a = P = K\sqrt{d},$$

where $K$ is a proportionality constant.

Again, the total length of fiber in the plug is

$$L = \frac{W}{d},$$

and the total surface area of all fibers in the plug is

$$A = La = \frac{W}{d} \cdot K\sqrt{d} = \frac{KW}{\sqrt{d}}.$$

The rate of air-flow for constant maturity is then

$$R = \frac{K'}{A} = \frac{K'K\sqrt{d}}{W},$$

and, since $W$ is fixed, is proportional to the square root of $d$ (*i.e.*, the square root of the fineness of the fibers).

Two curves following the square-root law are plotted in Figure 1 to represent high and low maturity values. It should be realized that points on a constant-maturity curve are given by different cottons.

These derivations show that variations in resistance to air-flow with changes in perimeter are different from those with changes in maturity, in that the first follows the first-power law while the second follows a square-root law.

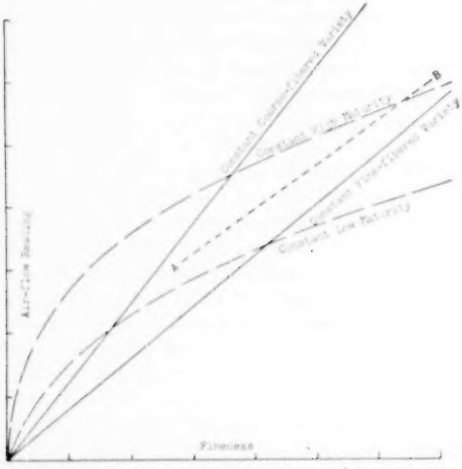


FIG. 1. *Theoretical curves for constant variety and constant maturity.*

## Experimental Procedure

For the experimental part of this study, two types of air-flow instruments were used:

Instrument A employed a very low rate of flow through a slightly compressed fiber plug. Air was forced through the sample with a pressure equivalent to 0.2 in. of oil. The rate of air-flow was measured by an oil manometer across a small orifice in series with the plug.

Instrument B used approximately 5 lbs. of pressure on a rather highly compressed fiber plug. The rate of flow was measured by a visible flowmeter of the rotameter type. The scale had previously been graduated in micrograms per inch. These divisions, however, could also be considered to form a linear scale for rate of air-flow, although such units were not attached.

Several cottons, representing an extreme range of maturities, were tested. The Bureau of Plant Industry, U.S.D.A., furnished samples of 7 common cottons harvested at 5-day intervals for 5 successive pickings, beginning at 30 days from the time of flowering.

For data on fineness and maturity obtained by the counting-and-weighing method, the samples were

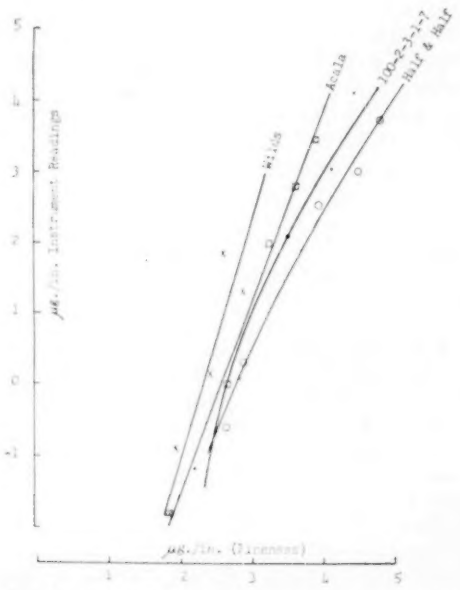


FIG. 2. *Constant-variety curves for several cottons.*

run by the U.S.D.A. Fiber and Spinning Laboratory at Clemson, South Carolina. The same samples were then carefully tested with the air-flow instruments A and B. The samples were fluffed and blended on a blender similar to that of Stewart [6]; 50 grains of fiber were carefully tested, first with instrument A, and then they were removed and placed in instrument B without refluffing. (It was found that refluffing did not change the results.) The whole series of samples were refluffed and run again a week later on both machines. The results for both of the repeat runs were surprisingly close to those for the original runs.

## Results

In Figures 2 and 3 are shown the actual readings of instrument B for constant variety. Note that the curves are nearly straight lines, which agree fairly well with constant-variety lines predicted by the theory. They do not go through the origin since the scale on this apparatus does not have its "zero" coincident with zero rate of flow. The apparently negative readings were obtained by extending the positive scale downward with the same-size divisions. It is seen that whereas the points for several of the cottons fall on curves close together extreme cottons give the same rate of air-flow although their actual finenesses differ by 1 or 2 micrograms per inch.

In Figure 4 are shown several "best fit" curves for constant maturity superimposed on the constant-variety curves taken from Figures 2 and 3. It is seen that the constant-maturity curves fit the points rather poorly but that they come nearer following the square-root law than they do the first-power variation. The two sets of curves form a pattern somewhat like that for the theoretical curves of Figure 1.

In the original calibration of instrument B, the scale had been chosen by using samples from several cottons in the usual range of maturity. This procedure is equivalent to using a calibration curve that follows neither constant-variety nor constant-maturity curves but cuts across both sets, as is roughly indicated by the dotted line A–B in Figure 1. It is clear that for all cottons the readings for fineness at very low maturities would be expected to be too low. This is found to be the case for all 7 cottons shown in Figures 2 and 3. Also, some cottons will register

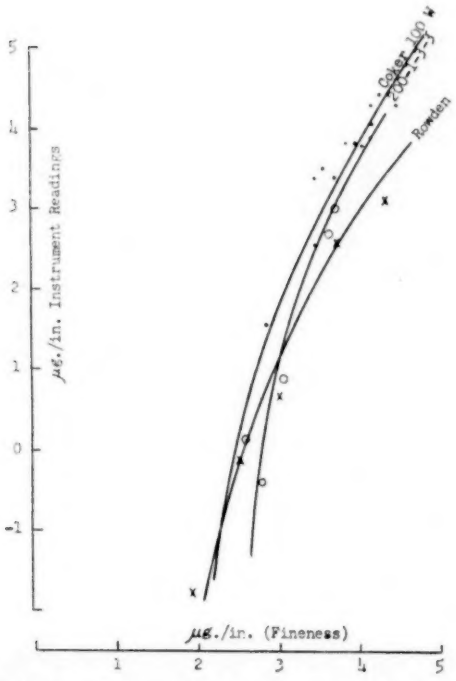


FIG. 3. *Constant-variety curves for several cottons.*

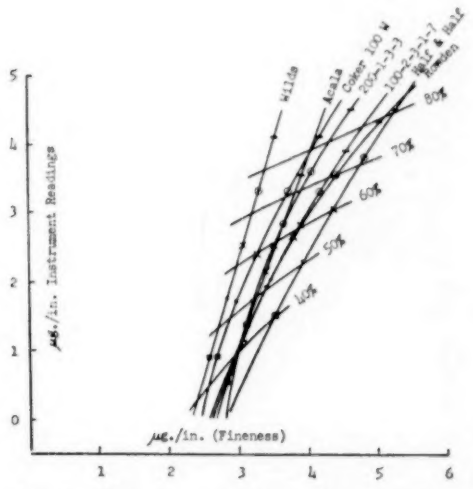


FIG. 4. *Maturity-variety diagram for all 7 cottons.*

too-high fineness at very high maturities. If a single calibration curve must be used, one which agrees with a constant-variety curve for a cotton like Acala (see Figure 4) would give small error for several other cottons and at least decrease the possible error for the more extreme varieties.

If the fiber perimeter is constant within a variety, variations in fineness are caused only by variations in maturity. In fact, either fineness or maturity is a measure of fiber development. Calibration curves which can be used for finding percent maturity from air-flow readings are shown in Figures 5 and 6.

Likewise, when working with a known variety, because of the common relationship between fineness and maturity, it is necessary to measure only one of these factors, since suitable curves (see Figures 7 and 8) for one can be used to find the other.

For the 1948 crop, the U.S.D.A. used an air-flow method to determine fineness, and the data on several varieties have been published. In the previous decade the fineness of some of the same varieties had been measured by counting and weighing the fibers. Table I shows the results for both methods. Here again, at low maturity the air-flow instrument gave values too low, as should be expected from using a single fineness scale for all varieties.

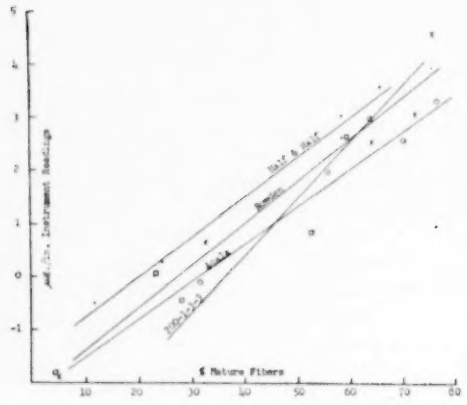


FIG. 5. *Variation of air-flow with percent maturity.*

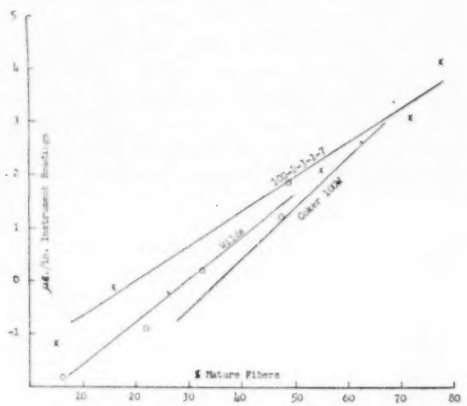


FIG. 6. *Variation of air-flow with percent maturity.*

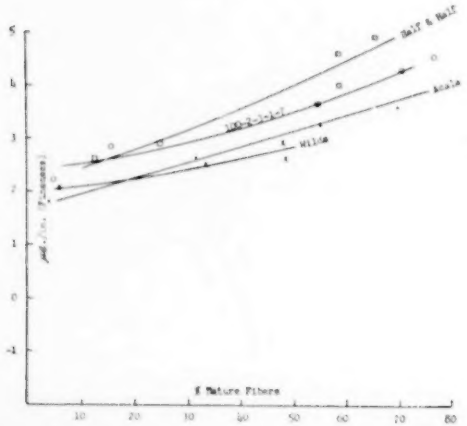


FIG. 7. *Variation of fineness with percent maturity.*

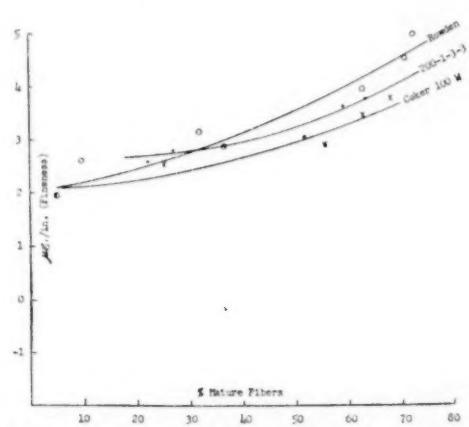


FIG. 8. *Variation of fineness with percent maturity.*

TABLE I. CORRELATION OF AIR-FLOW READINGS OF FINENESS WITH FINENESS AS DETERMINED BY WEIGHING AND % MATURITY *

| Variety | % Maturity | Fineness by air-flow Crop of 1948 µg./in. | Standard error of estimate | Fineness by weighing Crops of 1937–1947 † µg./in. | Standard error of estimate |
|---|---|---|---|---|---|
| | 75 | 4.14 | | 5.34 | |
| Rowden | 80 | 4.80 | .30 | 5.73 | .45 |
| | 85 | 5.45 | | 6.17 | |
| | 75 | 3.85 | | 4.15 | |
| Deltapine | 80 | 4.25 | .30 | 4.55 | .37 |
| | 85 | 4.66 | | 4.98 | |
| | 70 | 3.15 | | 3.92 | |
| Coker 100 W | 75 | 3.64 | .25 | 4.21 | .38 |
| | 80 | 4.12 | | 4.47 | |
| | 85 | 4.65 | | 4.78 | |
| | 70 | 3.31 | | 4.06 | |
| Stoneville 2B | 75 | 3.74 | .32 | 4.19 | .37 |
| | 80 | 4.16 | | 4.31 | |
| | 85 | 4.60 | | 4.43 | |
| | 70 | 3.48 | | 3.65 | |
| Acala | 75 | 3.82 | .20 | 3.81 | .25 |
| | 80 | 4.17 | | 4.02 | |
| | 85 | 4.48 | | 4.26 | |

* From data published by U. S. D. A.
† Not every variety listed was planted and tested each year.

The data in Table I can be used to plot separate curves for each variety, showing variation of maturity and fineness with air-flow readings. With these curves, maturity and fineness both may be determined from air-flow readings alone.

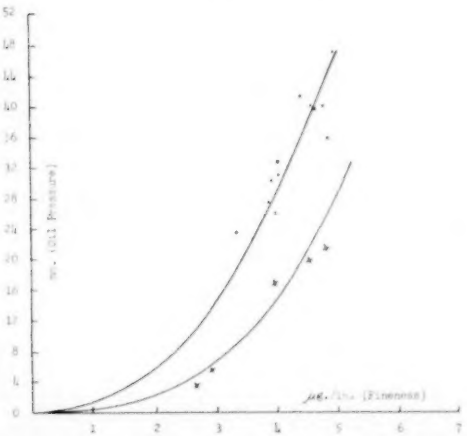

FIG. 9. *Variation in air-flow readings with fineness.*

The columns headed "standard error of estimate" give the required plus or minus spread from the mean curves to include two-thirds of the original readings.

In the course of this study a large amount of data published during the past 10 years by the U.S.D.A. were summarized. There were sufficient data on 24 different cottons to plot with reasonable accuracy curves showing the variation of fineness with maturity. The curves were drawn by eye to fit the points as well as possible. The "standard error of estimate" was determined by finding the deviation from the curve to include one-third of the points on each side of the line. Table II lists a sufficient number of points from the curves themselves for replotting them. Such curves will give fineness from maturity reading (or vice versa) with an accuracy indicated by the approximated error of estimate. It is surprising that the error of estimate is so low when it is realized that the data published will have variations due to season and weather, locality of growth, time of picking, and variation in purity of strain, besides the errors inherent in testing in several different laboratories. That the spread is so small seems to be evidence of good testing consistency over

TABLE II. CORRELATION OF FINENESS AND MATURITY *

| Variety | % Maturity: % Mature fibers | % Maturity: Standard error of estimate | Fineness by weighing Crops of 1937–1947 †: μg./in. | Fineness by weighing Crops of 1937–1947 †: Standard error of estimate |
|---|---|---|---|---|
| | 65 | | 5.10 | |
| Half & Half | 70 | 5 | 5.40 | .45 |
| | 75 | | 6.00 | |
| | 80 | | 6.81 | |
| | 50 | | 3.00 | |
| | 55 | | 3.21 | |
| Wilds | 60 | 9 | 3.41 | .25 |
| | 65 | | 3.57 | |
| | 70 | | 3.68 | |
| | 75 | | 3.76 | |
| | 60 | | 3.70 | |
| | 65 | | 3.95 | |
| Deltapine 11 | 70 | 5 | 4.25 | .37 |
| | 75 | | 4.60 | |
| | 80 | | 5.07 | |
| | 75 | | 3.90 | |
| Deltapine 14 (060) | 80 | 5 | 4.34 | .38 |
| | 85 | | 4.88 | |
| | 70 | | 4.06 | |
| Deltapine 14 (833) | 75 | 7 | 4.38 | .37 |
| | 80 | | 4.70 | |
| | 85 | | 5.03 | |
| | 60 | | 4.11 | |
| | 65 | | 4.35 | |
| Stoneville 5 | 70 | 12 | 4.55 | .37 |
| | 75 | | 4.68 | |
| | 80 | | 4.78 | |
| | 65 | | 3.40 | |
| Stoneville 2B (8275) | 70 | 15 | 3.82 | .37 |
| | 75 | | 4.22 | |
| | 80 | | 4.65 | |
| | 60 | | 3.97 | |
| | 65 | | 4.33 | |
| Hibred | 70 | 7 | 4.73 | .45 |
| | 75 | | 5.14 | |
| | 80 | | 5.60 | |
| | 85 | | 6.08 | |
| | 55 | | 4.10 | |
| | 60 | | 4.38 | |
| | 65 | | 4.63 | |
| Qualla | 70 | 5 | 4.88 | .23 |
| | 75 | | 5.10 | |
| | 80 | | 5.28 | |
| | 85 | | 5.45 | |
| | 50 | | 3.65 | |
| | 55 | | 3.82 | |
| Delfos (Mesdell 4) | 60 | 9 | 4.00 | .30 |
| | 65 | | 4.15 | |
| | 70 | | 4.30 | |
| | 75 | | 4.43 | |

TABLE II—*Continued*

| Variety | % Maturity: % Mature fibers | % Maturity: Standard error of estimate | Fineness by weighing Crops of 1937–1947 †: μg./in. | Fineness by weighing Crops of 1937–1947 †: Standard error of estimate |
|---|---|---|---|---|
| | 65 | | 4.45 | |
| Startex | 70 | 4 | 4.82 | .50 |
| | 75 | | 5.30 | |
| | 80 | | 6.05 | |
| | 65 | | 4.10 | |
| | 70 | | 4.32 | |
| Mexican Big Bowl | 75 | 8 | 4.59 | .45 |
| | 80 | | 4.88 | |
| | 85 | | 5.18 | |
| | 55 | | 4.17 | |
| | 60 | | 4.41 | |
| Farm Relief | 65 | 5 | 4.68 | .26 |
| | 70 | | 4.95 | |
| | 75 | | 5.15 | |
| | 80 | | 5.32 | |
| | 60 | | 4.55 | |
| | 65 | | 4.90 | |
| Cleveland | 70 | 15 | 5.16 | .37 |
| (Wannamaker) | 75 | | 5.30 | |
| | 80 | | 5.36 | |
| | 85 | | 5.45 | |
| | 60 | | 3.70 | |
| | 65 | | 3.85 | |
| Arkansas | 70 | 8 | 4.08 | .40 |
| | 75 | | 4.34 | |
| | 80 | | 4.67 | |
| | 65 | | 4.25 | |
| | 70 | | 4.52 | |
| Cook 912 | 75 | 5 | 4.81 | .25 |
| | 80 | | 5.10 | |
| | 85 | | 5.45 | |
| | 60 | | 3.45 | |
| | 65 | | 3.72 | |
| Rogers Acala | 70 | 9 | 3.95 | .35 |
| | 75 | | 4.13 | |
| | 80 | | 4.30 | |
| | 65 | | 4.56 | |
| Triumph (759) | 70 | 5 | 4.85 | .37 |
| | 75 | | 5.15 | |
| | 80 | | 5.48 | |
| | 60 | | 4.10 | |
| | 65 | | 4.47 | |
| Triumph (44) | 70 | 5 | 4.83 | .37 |
| | 75 | | 5.23 | |
| | 80 | | 5.70 | |

* From data published by the U.S.D.A., 1937–47.

† Not every variety listed was planted and tested each year.

a period of several years. It will be found that some of these lines bend one way and some the other. This is to be expected, since the rate of growth of cellulose in a given sample of cotton will follow an "S" curve, owing mainly to the fact that not all the fibers start (or finish) their growth at the same time. Whether the curve will be concave upward or downward depends upon what stage of the wall development is represented by the sample. In general, for low-maturity samples, the curve is concave upward, and for samples of high maturity, the curve is concave downward.

The results for instrument A were parallel throughout with those for instrument B. Figure 9 shows manometer readings of instrument A plotted against actual values of fineness for the two cottons that gave the most divergent curves for instrument B. (The lines are curved, since the manometer readings do not vary linearly with rate of air-flow.) Again, cottons differing 1 or 2 micrograms in fineness give identical readings on the air-flow apparatus. It is believed that this will be true of any instrument based on the air-flow principle.

## Conclusions

1. It seems that, theoretically and practically, air-flow methods give readings that correlate much better with specific surface than with fineness or maturity. If calibrated in units of specific surface, it seems that any of the air-flow instruments will measure all cottons with one curve (or scale).

2. For single varieties of cotton, both fineness and maturity may be found from air-flow readings, thus eliminating the old, tedious tests for these properties when extreme accuracy is not required.

3. For several varieties of cotton, published data can be used to establish correlation curves between fineness and maturity. These curves will give, with fair accuracy, either property from measurements on the other. This eliminates the need for one tedious operation.

4. For unknown cottons, an air-flow test plus a measurement of either fineness or maturity will give the other. Quite often, maturity measurements will be made regardless and can be used in conjunction with air-flow data to give practical values for fineness.

5. It is believed the air-flow method is sound and that, within their limitations, the several instruments are very worth-while, time-saving devices. Since they seem to measure specific surface directly, it would be fortunate if this factor were as good as fineness for predicting spinning characteristics and yarn quality.

However, especially in the higher counts, since weight per inch determines the number of fibers in a yarn cross section, it seems that fineness will indicate yarn properties better than specific surface will. Cottons having the same specific surface may differ as much as 2 to 1 in number of fibers per cross section in a given yarn and would, therefore, have quite different spinning characteristics.

## Acknowledgment

The authors wish to give credit to Mr. Murphy Cook, of the U.S.D.A. Laboratory at Clemson; Dr. Thomas Kerr, of the Bureau of Plant Industry; and Dr. A. N. J. Heyn, of this laboratory, for valuable aid in providing samples, experimental data, and helpful advice.

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# Some Comparisons of Fiber "Fineness" Measurements

**Edward W. S. Calkins***


## Abstract

Interlaboratory check tests show excellent correlation between our homemade air-permeability instrument and both the University of Tennessee's "Arealometer" and an air-permeability instrument in another laboratory. From similar results reported by other investigators for their own instruments, it is concluded that any instrument of this type if properly calibrated can do a good job of measuring surface area.†

Comparison of data found in the literature on normal fiber perimeter, wall thickness, surface area, and weight per inch with calculated values indicates that all laboratory measurements of fiber dimensions are surprisingly accurate and consistent. Drawings of fiber cross sections with various combinations of dimensions indicate that fibers with the same surface area are most alike in appearance and ought to be more alike in their spinning behavior than those selected for uniformity by any other fineness measurement. A chart is given (Figure 5) from which any two of the four fineness variables can be read if the other two are known.

It is shown that fibers of the same surface area may vary widely in weight per inch, and that no conversion from surface area to weight per inch can be accurate unless one other variable is held constant. This may be either wall thickness, fiber diameter, or their ratio, usually called "maturity."


## Interlaboratory Check Tests

In September, 1947, when our homemade fiber-fineness tester was being calibrated, 11 samples of cotton covering a range of manometer readings from .42 to .82, or nearly 2 to 1, were sent to the University of Tennessee for measurement on Dr. K. L. Hertel's Arealometer. The results are shown in Table I and Figure 1. The coefficient of correlation is .9833, and after our manometer readings were converted to surface area by the use of the formula for the straight line shown on the chart, the average difference between surface areas obtained by the two instruments was .049 square centimeter per mg., or less than 2%. Most of this variation is attributed to sampling and could be reduced by taking five or ten readings on each sample instead of two, but we decided that two gave sufficient accuracy for our purposes.

Recently another check test was made, this time between our instrument and an instrument of the air-permeability type in another laboratory, which had been calibrated in weight per in., and which will be called "Instrument B" throughout the remainder of this paper. This time 10 samples were tested and the coefficient of correlation was .984, or almost exactly the same as that obtained with the Arealometer. Table II and Figure 2 compare the readings on these 10 samples.*

Since Hertel and Sullivan proved conclusively 10 years ago that what the Arealometer measures is area per unit of weight or volume, we take these high correlations to mean that our instrument and Instrument B also measure surface area, and with approximately the same degree of consistency as the Arealometer. Other workers have shown similar correlations between their own air-permeability instruments and the Arealometer, and it seems safe to generalize that any instrument which measures the resistance of a wad of cotton to the flow of air can

* Cotton Fiber Technologist, United States Rubber Company, New York.

† To be understood in scientific fields outside the textile industry, we should say "specific surface" instead of "surface area." However, the term "surface area" is commonly employed in the textile industry to mean fiber surface in square centimeters per milligram of sample weight, and it is so used in this paper.

* These two interlaboratory comparisons were conducted by Messrs. E. A. McMaster and T. E. Neal of the United States Rubber Company's Central Development Department, Winnsboro, S. C.

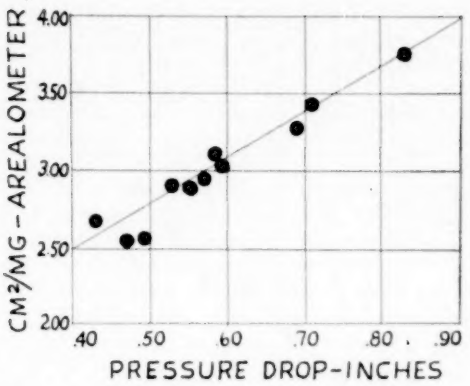


FIG. 1. *Comparison of University of Tennessee surface area with U. S. Rubber Co. manometer readings.*

TABLE I. INTERLABORATORY CHECK TEST, 1947

| Sample No. | Arealometer Surface area * (cm.²/mg.) | U. S. Rubber Co. Instrument Manometer reading | U. S. Rubber Co. Instrument Surface area † (cm.²/mg.) |
|---|---|---|---|
| 1 | 2.550 | .460 | 2.660 |
| 2 | 3.050 | .585 | 3.035 |
| 3 | 3.755 | .825 | 3.755 |
| 4 | 2.645 | .425 | 2.555 |
| 5 | 2.525 | .465 | 2.675 |
| 6 | 2.890 | .530 | 2.870 |
| 7 | 3.270 | .690 | 3.350 |
| 8 | 2.875 | .550 | 2.930 |
| 9 | 3.065 | .585 | 3.035 |
| 10 | 3.420 | .705 | 3.395 |
| 11 | 2.925 | .570 | 2.990 |

* Average of two readings.
† Three times manometer reading plus 1.28.

be calibrated to read in units of surface area, or that the readings of whatever meter is on the instrument can be converted to surface area by the use of simple charts or conversion formulas.* This was done very easily for our own instrument by comparing its readings with the University of Tennessee measurements on the same samples.

### Agreement of Calculated and Observed Values

Table III shows normal or average values for fiber perimeter, wall thickness, weight per inch, and surface area for a number of cotton varieties, collected from various reports of the U. S. Department of Agriculture. From the perimeter and wall thickness, it is a matter of simple arithmetic to calculate the outside and inside diameters, cross-sectional area, volume, and weight per inch of straight fibers of circular cross section. The fact that cotton fibers are not straight, perfectly round tubes does not affect the accuracy of these results. If there is any doubt on this point, one may take a piece of copper tubing of any convenient diameter and length, weigh it, measure its outside cylindrical surface, and then flatten it and twist it into a shape approximating that of a cotton fiber. Obviously there will have been no

* It has not been proved that this is true over the entire possible range of sample densities and air pressures that might be employed, but the relationships seem to hold under the usual test conditions.

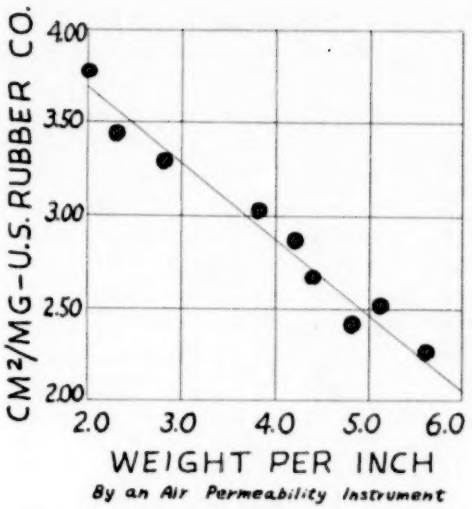


FIG. 2. *Comparison of U. S. Rubber Co. surface area with "weight per inch" by Instrument B.*

TABLE II. INTERLABORATORY CHECK TEST, 1949

| Sample No. | U. S. Rubber Co. Instrument Surface area (cm.²/mg.) | Instrument B "Weight per inch" (μg.) |
|---|---|---|
| 1 | 2.27 | 5.6 |
| 2 | 2.42 | 4.8 |
| 3 | 2.51 | 5.1 |
| 4 | 2.66 | 4.4 |
| 5 | 2.87 | 4.2 |
| 6 | 3.02 | 3.8 |
| 7 | 3.29 | 2.8 |
| 8 | 3.44 | 2.3 |
| 9 | 3.77 | 2.0 |
| 10 | 4.10 | Below scale |

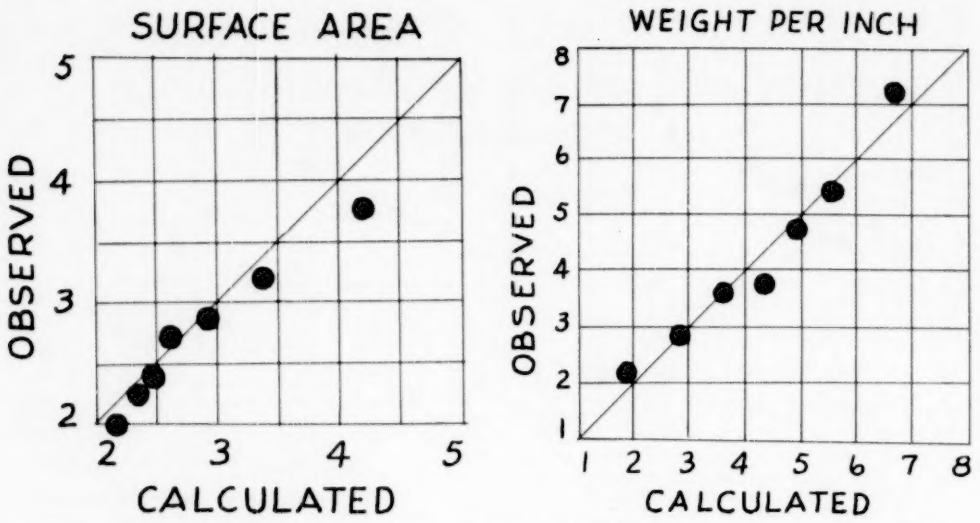


FIG. 3. *Comparison of observed and calculated values for surface area and weight per inch from Table III.*

change in its weight or length; hence its weight per inch is the same. If the area of the irregularly flattened and twisted tube can be measured with sufficient accuracy, it will be found not to have changed, since there must be somewhere around the perimeter of the tube exactly 360 degrees of curvature, making the difference between the inside and outside perimeters equal to 3.1416 times twice the wall thickness. As long as the wall thickness remains unchanged, the perimeter halfway between the outer and inner surfaces of the wall cannot change, and any stretching of the outer surface where the curvature is increased is balanced by an equal compression at places where the wall has been flattened. This is approximately what happens when a cotton fiber, which has grown as a round tube in the unopened boll, dries out and collapses. There is, of course, some lateral shrinkage, which need not concern us so long as we are dealing only with the dimensions of dried fibers. Thus, the assumption of a perfect cylindrical shape does not measurably affect the accuracy of the final figures, but greatly simplifies the calculations.

A comparison of the calculated and observed values for surface area and weight per inch in Table III shows remarkably close agreement, which is demonstrated graphically in Figure 3. This gives us more confidence in both the laboratory measurements and the calculations.

It has been thought that measurements of the dimensions of the fiber cross section under the micro-

TABLE III. OBSERVED AND CALCULATED VALUES FOR NORMAL WEIGHT PER INCH AND SURFACE AREA OF VARIOUS COTTONS

| Variety | Perimeter (μ) | Diameter (μ) | Wall thickness (μ) | Weight per inch (μg.) calc. | obs. | Surface area (cm.²/mg.) calc. | obs. |
|---|---|---|---|---|---|---|---|
| Sea Island | 31.42 | 10 | 2.0 | 1.92 | 2.2 | 4.16 | 3.75 |
| Wilds | 37.70 | 12 | 2.5 | 2.85 | 2.9 | 3.36 | 3.20 |
| Acala | 40.84 | 13 | 3.0 | 3.60 | 3.6 | 2.89 | 2.85 |
| Stoneville, Delta & Pine Land, Coker | 43.98 | 14 | 3.4 | 4.32 | 3.8 | 2.59 | 2.72 |
| Half & Half | 47.12 | 15 | 3.6 | 4.92 | 4.8 | 2.43 | 2.40 |
| Rowden | 50.27 | 16 | 3.8 | 5.56 | 5.5 | 2.30 | 2.25 |
| Indian | 56.55 | 18 | 4.0 | 6.72 | 7.2 | 2.14 | 2.00 |
| Coarse Asiatic | 65.97 | 21 | 6.0 | 10.80 | — | 1.55 | — |

scope were subject to some errors in magnification or focusing, that surface-area measurements were affected to some extent by the "shape factor," and that weight-per-inch determinations could be thrown far off the track by imperfect sorting and the failure of the technician to reject any fibers that were not exactly the right length. In spite of all these possible errors, the agreement between observed and calculated values is surprisingly good. With these five interrelated variables, each subject to possible errors from entirely independent causes, the chances are extremely small that the results might agree if any of the errors were of appreciable magnitude. It must be concluded that all our laboratory measurements are probably much more accurate than generally believed.

### Interrelation of Fineness Measurements

In Table IV are given the calculated weight per inch and the surface area for a series of fibers of varying diameter and wall thickness. Some of these are illustrated by circular cross-section sketches in Figure 4. In the top row there are three fibers of the same diameter but of different wall thickness, and their surface area and weight per inch are noted beside each. The second row shows fibers of the same wall thickness and different diameters; it will be noted that there is much less variation in surface area than in weight per inch. This makes it appear that as a measure of wall thickening, or maturity, surface area is better than weight per inch. As further proof of this, there are in the third row fibers of the same weight per inch, which vary 2 to 1 in diameter and surface area and 3 to 1 in wall thickness. Nowhere on the chart, in the writer's opinion, are there three fibers which look less alike, which shows that when we measure only weight per inch we have no idea what the fibers are really like or what their spinning behavior should be. For instance, the one on the right might be an unusually mature Sea Island or Karnak which would make fine strong yarns with very few neps, while the large, thin-walled fiber on the left might represent, in slightly exaggerated form, an immature Rowden, the victim of a drought such as is seldom experienced in the areas where Rowden is grown. Its spinning behavior can be imagined from

TABLE IV. CALCULATED WEIGHT PER INCH AND SURFACE AREA FOR VARIOUS FIBER DIAMETERS AND WALL THICKNESSES

| Diameter ($\mu$) | Perimeter ($\mu$) | Wall thickness ($\mu$) | Weight per inch ($\mu$g.) | Surface area (cm.²/mg.) |
|---|---|---|---|---|
| 20 | 62.83 | 4.0 | 7.68 | 2.08 |
| 20 | 62.83 | 2.5 | 5.25 | 3.05 |
| 20 | 62.83 | 2.0 | 4.32 | 3.71 |
| 20 | 62.83 | 1.72 | 3.80 | 4.20 |
| 20 | 62.83 | 1.5 | 3.33 | 4.80 |
| 20 | 62.83 | 1.27 | 2.85 | 5.60 |
| 20 | 62.83 | 1.0 | 2.28 | 7.02 |
| 18 | 56.55 | 3.0 | 5.40 | 2.66 |
| 15 | 47.12 | 5.0 | 6.00 | 2.00 |
| 15 | 47.12 | 4.0 | 5.28 | 2.26 |
| 15 | 47.12 | 2.8 | 4.09 | 2.93 |
| 15 | 47.12 | 2.5 | 3.75 | 3.20 |
| 15 | 47.12 | 2.0 | 3.12 | 3.84 |
| 15 | 47.12 | 1.8 | 2.85 | 4.20 |
| 15 | 47.12 | 1.5 | 2.42 | 4.93 |
| 15 | 47.12 | 1.0 | 1.68 | 7.12 |
| 10 | 31.42 | 5.0 | 3.00 | 2.66 |
| 10 | 31.42 | 4.0 | 2.88 | 2.78 |
| 10 | 31.42 | 3.9 | 2.85 | 2.80 |
| 10 | 31.42 | 2.5 | 2.25 | 3.55 |
| 10 | 31.42 | 2.0 | 1.88 | 4.24 |
| 10 | 31.42 | 1.98 | 1.90 | 4.20 |
| 10 | 31.42 | 1.0 | 1.08 | 7.40 |
| 5 | 15.71 | 2.0 | .72 | 5.56 |
| 5 | 15.71 | 1.0 | .48 | 8.33 |

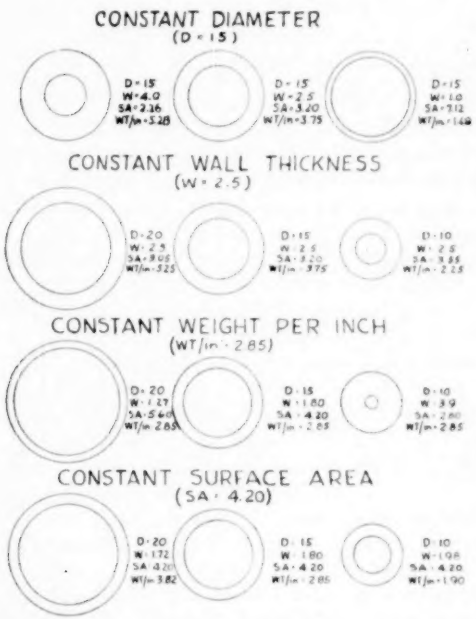


FIG. 4. *Effect of holding one fiber measurement constant and varying others.*

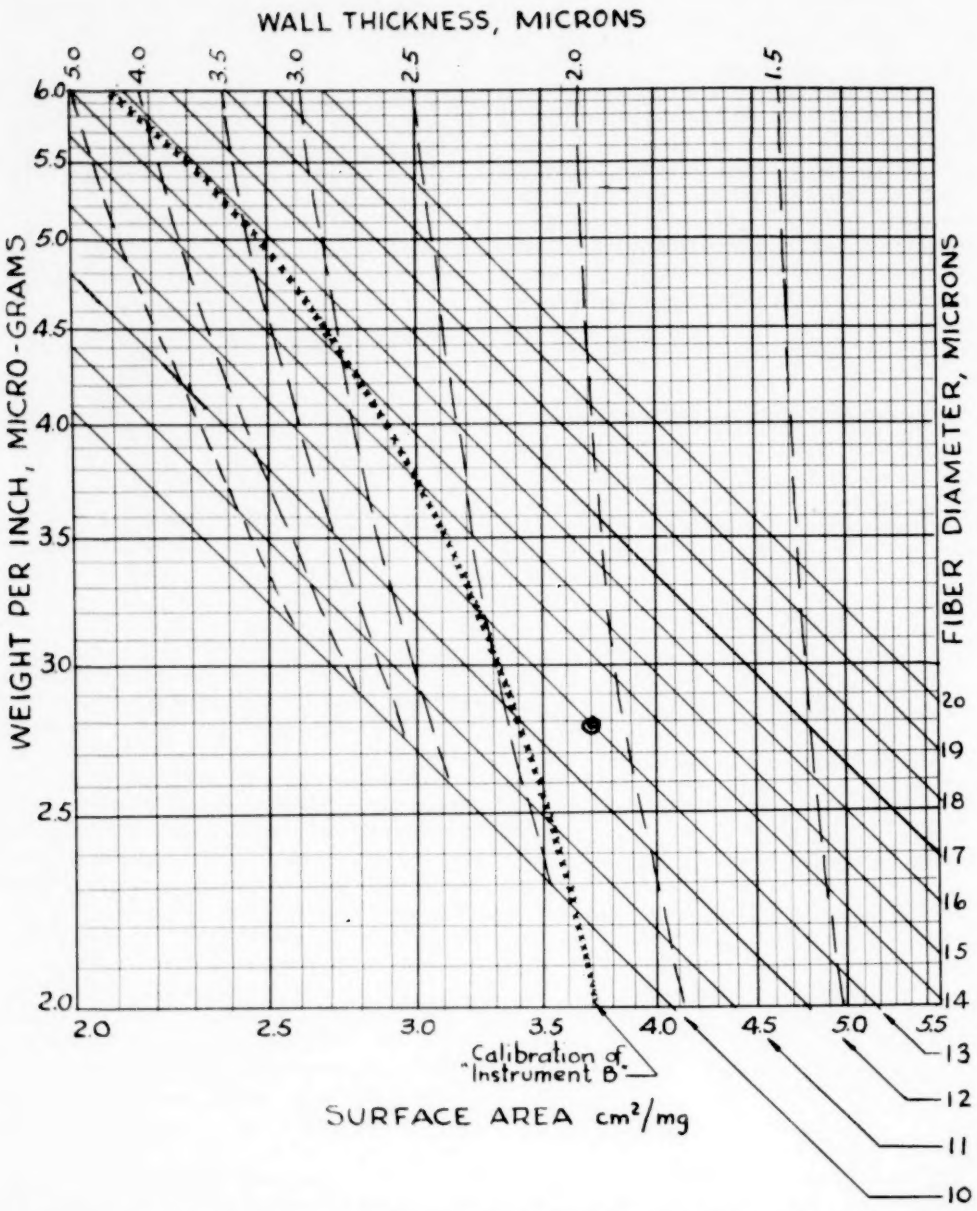


FIG. 5. *Relation of surface area to weight per inch for fibers of various diameters and wall thicknesses.*

its large surface area; such fibers would give a dusty card room and excessive waste, require frequent stripping of the cards, and produce poor running conditions and neppy yarn. The center fiber is typical of the rather immature first pickings in the Mississippi Delta in 1948, in fields where the bolls opened early because of hot, dry weather. The fibers in the bottom row have the same surface area and nearly the same wall thickness and probably look more alike than any other three fibers on the page. We believe that they would spin about alike in spite of a 2 to 1 difference in diameter and weight per inch.

In Figure 5 are plotted the surface area and weight per inch of various fibers from Table IV. The points representing fibers of the same diameter have been connected by diagonal lines, and those with the same wall thickness by the nearly vertical, sloping, broken lines. From this chart it is seen that each different diameter requires a different conversion factor for estimating weight per inch from surface area. If we know only the surface area, our fiber is located definitely on one of the vertical lines of the chart, and if only the weight per inch is known, the sample may fall at any point on one of the horizontal lines; if both are known, there is only one possible point where it may fall—at the intersection of the two lines—and fiber diameter and wall thickness may then be estimated with fair accuracy. In some cases, it should be possible to identify the variety, or at least, as in the case of blood tests for paternity, to say definitely who was not the child's parent, and who might have been. It should be noted that this chart is plotted on a logarithmic scale. In the more common, equally spaced, rectangular-coordinate plot, the diagonal straight lines would become a series of hyperbolas. The curving line of crosses represents the "weight per inch" calibration of Instrument B taken from Table II and is the same as the straight line in Figure 2. Sample No. 9 (Table II), with a surface area of 3.77 was known to be an immature Acala which had opened late in the season because of frost. As measured by Instrument B, this sample has a weight per inch of 2.0 micrograms, which corresponds to a fiber diameter of 9.0 microns. Since the cotton was an Acala, it is safe to assume that its diameter was really about 13 microns, which raises the point to the dot which is marked by a small circle on the chart. Following the horizontal line over to the left from this point, we find that the weight per inch ought to have been 2.8 instead of 2.0, an error of 30%.*

In the Appendix are details of the method of calculating surface area and weight per inch and also some simplified formulas for calculating fiber diameter and wall thickness if both surface area and weight per inch are known. Since surface area times weight per inch is equal to four-fifths of the fiber diameter in microns, it is obvious that no correlation between surface area and weight per inch is possible except for a series of samples specially selected for uniform fiber diameter, wall thickness, or maturity.

Our calibration curve for Instrument B (Figure 5) shows consistently decreasing diameter and wall thickness with decreasing indicated weight per inch, and the ratio of diameter to wall thickness seems to remain pretty consistently between 4 and 5, which suggests that its original calibration was based on a series of well-matured samples of different varieties and hence of different fiber diameters, probably ranging from Sea Island or Wilds to Rowden. If the calibration had been the result of testing only samples of the Stoneville, Deltapine, and Coker varieties of varying degrees of maturity, an entirely different scale would have resulted, which would have been accurate within about 7% for nine-tenths of the commercial crop, and might have been more useful in the average fiber testing laboratory. However, the only correct scale for these air-permeability instruments is a surface-area scale, and the assumption that they can measure anything else is sure to result in serious errors on some samples. This should not be misunderstood as meaning that air-permeability instruments are not suitable for general laboratory use; those available commercially, as well as most of the homemade instruments which have been described in the literature appear to be well designed and well built, and they all appear to give reproducible results and to be great time savers. Those which have been calibrated in units of weight per inch could

* After these calculations were made and this paper had been read at the A.S.T.M. meeting in Philadelphia, the sample was tested in the laboratory of the U. S. Department of Agriculture at Stoneville, Mississippi, and the weight per inch by the array method was reported to be 3.0 micrograms; this is 50% higher than had been indicated by the air-permeability instrument.

very easily * be fitted with a new scale to read surface area correctly instead of weight per inch incorrectly. There are a few other instruments which use various fineness indexes or arbitrary scale readings (only one of a kind), which have no meaning except to those familiar with their use. It is suggested that it would be of some benefit to the fiber-testing fraternity if these were recalibrated to read surface area so that all users who have occasion to compare results would be speaking the same language.

It is recognized that for solid fibers, such as wool, rayon, nylon, etc., an air-permeability instrument can be calibrated to read in denier or any other unit that is customarily used for the fiber concerned, the only precaution being that the same denier scale cannot be used for all fibers because of differences in specific gravity and shape of cross section. This difficulty can be overcome for circular fibers by varying the sample weight in proportion to specific gravity, or for any fiber by measuring a series of samples of known fineness.

## *Appendix*

### Method of Calculating Weight per Inch and Surface Area

Given: Fiber perimeter ($P$) or outside diameter ($D$) in microns and wall thickness ($T$) in microns

$P = 3.1416D$ microns

Inside diameter ($D_i$) $= D - 2T$ microns

Cross-sectional area of wall ($A$) $= .7854D^2 - .7854D_i^2$ square micron

Volume ($V$) of 1-inch length of fiber $= 25{,}400A$ cubic microns

Density of cellulose = 1.5

Weight of 1 cubic micron of cellulose = .0000015 microgram

Weight per inch ($W$) $= .0000015V$ microgram $= .0381A$ microgram

Outside surface ($S$) of 1-inch length of fiber $= 25{,}400P$ square microns

Surface per unit of weight $= \frac{S}{W}$ square microns per microgram

1 milligram = 1,000 micrograms

1 square centimeter = 100,000,000 square microns

Surface area expressed in square centimeters per milligram $= \frac{1000S}{100{,}000{,}000W}$

or $.00001\,\frac{S}{W}$

Note: The calculation is simplified by cancelling out some of the factors before beginning the computation. Obtain $P$ and $A$ as above; then,

$$\text{Surface area} = \frac{20P}{3A}$$

$$W = .0381A$$

$$\text{Surface area} = \frac{0.797D}{W}$$

From the above, if surface area and weight per inch have been measured, fiber diameter and wall thickness can be estimated:

$D$ = Surface area × weight per inch × 1.255

$A$ = 26.25 × weight per inch

$D_i = \sqrt{1.273(.7854D^2 - A)}$

$$T = \frac{D - D_i}{2}$$

*Examples*

Given: $D = 15$ microns and $T = 2$ microns:

$P = 47.12$ microns

$D_i = 11$ microns

$A = .7854(225 - 121) = 81.7$ square microns

Long method:

$V = 25{,}400 \times 81.7 = 2{,}080{,}000$ cubic microns

$W = 3.12$ micrograms

$S = 25{,}400 \times 47.12 = 1{,}200{,}000$ square microns

$\frac{S}{W} = \frac{1{,}200{,}000}{3.12} = 387{,}000$ square microns per microgram

Surface area $= .00001\,\frac{S}{W} = 3.87$ square centimeters per milligram

* This is easy only if a series of samples of known surface area is available for the calibration. Fortunately, the very difficult job of correctly calibrating the first surface-area instrument was done for us at the University of Tennessee, and does not need to be repeated by the ordinary commercial laboratory or instrument builder.

Short method:

$$W = .0381 \times 81.7 = 3.12 \text{ micrograms per inch}$$

$$\text{Surface area} = \frac{20 \times 47.12}{3 \times 81.7} = \frac{942.4}{245.1} = 3.87 \text{ cm.}^2/\text{mg.}$$

or

$$\text{Surface area} = \frac{.797 \times 15}{3.12} = 3.87 \text{ cm.}^2/\text{mg.}$$

Given: Surface area = 3.87 square centimeters per milligram

and $W = 3.12$ micrograms:

$$D = 3.87 \times 3.12 \times 1.255 = 15 \text{ microns}$$

$$A = 26.25 \times 3.12 = 81.7 \text{ square microns}$$

$$D_i = \sqrt{1.273(.7854 \times 255 - 81.7)} = 11 \text{ microns}$$

$$T = \frac{15 - 11}{2} = 2 \text{ microns}$$

(Manuscript received December 21, 1949.)

# Improvement of Cotton Fiber Properties by Plant Breeding*

J. Winston Neely†

AT THE TURN of the century when the cotton boll weevil threatened the American cotton industry, the breeders met the challenge by developing high-yielding varieties that matured early and escaped complete devastation. When fusarium wilt became prevalent in many parts of the Cotton Belt and made production unprofitable, if not impossible, on large areas, the breeders developed wilt-tolerant varieties that produced economic yields despite the presence of the wilt organism in the soil. More recently, mill operators, and, in turn, cotton producers, have called upon breeders for varieties with improved fiber properties and better manufacturing performance. This is a challenge that has been accepted by the cotton breeders, and they have geared their cotton breeding programs to meet this demand.

The improvement of the quality of cotton fiber through the development of improved varieties by breeding requires a full understanding of: (1) the physical basis of inheritance, (2) the origin and development of the cotton fiber, (3) the effect of inheritance and environment upon the properties of cotton fiber, (4) the use of fiber technology in the improvement of fiber quality through breeding, and (5) the use of plant breeding technique in developing improved cotton varieties.

## 1. Physical Basis of Inheritance

The seed of higher-order plants is the result of the union of two sexual cells or gametes. The male gametes are produced in the anthers while the female gametes are produced in the ovary. The male gametes might be called sperms or microspores and the female gametes eggs or megaspores. Each gamete, male or female, contains dark-staining bodies known as chromosomes. The chromosomes are located in the nuclei and at certain stages they are visible under the microscope. Generally speaking, the number of chromosomes in the male and female gametes is the same. Furthermore, the number is constant for a species or for a uniform agricultural variety. The chromosome number of each of the gametes is referred to as being $n$, or haploid. Each chromosome carries a large number of genes which are linearly arranged and which determine the development of inherited characteristics.

The production of male and female gametes and

* Presented at the meeting of the Fiber Society, Lowell Textile Institute, Lowell, Mass., Sept. 8, 1949.

† Plant Breeder, Stoneville Pedigreed Seed Company, Stoneville, Miss.

the process of sexual fertilization are illustrated in Figure 1, in which the life history of the corn plant is diagrammed. The corn plant is used as an illustration because the male and female gametes are produced in different parts of the plant.

The growing corn plant is designated as a sporophyte and each of its body cells contain $2n$ chromosomes. The male gametes are produced in the anthers, which are borne in the tassel. The female gametes are produced in the ovaries, which are found in the kernels on the ears.

The development of the mature pollen grain is the result of a series of cell divisions and reductions in which one microsporocyte, or mother-cell, with $2n$ chromosomes is transformed into several pollen grains with $n$ chromosomes. Inside the pollen grain 3 nuclei, 1 tube nucleus and 2 sperm nuclei, develop. Each sperm nucleus contains $n$ chromosomes.

The female gametes are developed in the ovary simultaneously with the development of the pollen grains. The development of each ovule is the result of a series of cell divisions and reductions in which each megasporocyte with $2n$ chromosomes is transformed into an embryo sac containing several nuclei. The functional nuclei are the single-egg nucleus and two polar fusion nuclei each with $n$ chromosomes.

When the pollen grains are mature they fall from the anthers to the style of the pistil, where they germinate. The style of the corn flower is commonly called the silk. Upon germination, the pollen tube grows down the style and one of the sperm nuclei combines with the two polar fusion nuclei to form the endosperm nucleus with $3n$ chromosomes. The other sperm nucleus combines with the egg nucleus to form the zygote with $2n$ chromosomes. The endosperm nucleus becomes the endosperm of the seed, which is stored food, and the zygote becomes the embryo. The following season the seed is planted and the embryo germinates, utilizes the food of the endosperm, and develops into the sporocyte of the following generation. The transfer of pollen from the anthers to the style of the ovary is known as pollination. The union of male and female gametes is known as fertilization.

When the zygotes are produced by self-pollinating

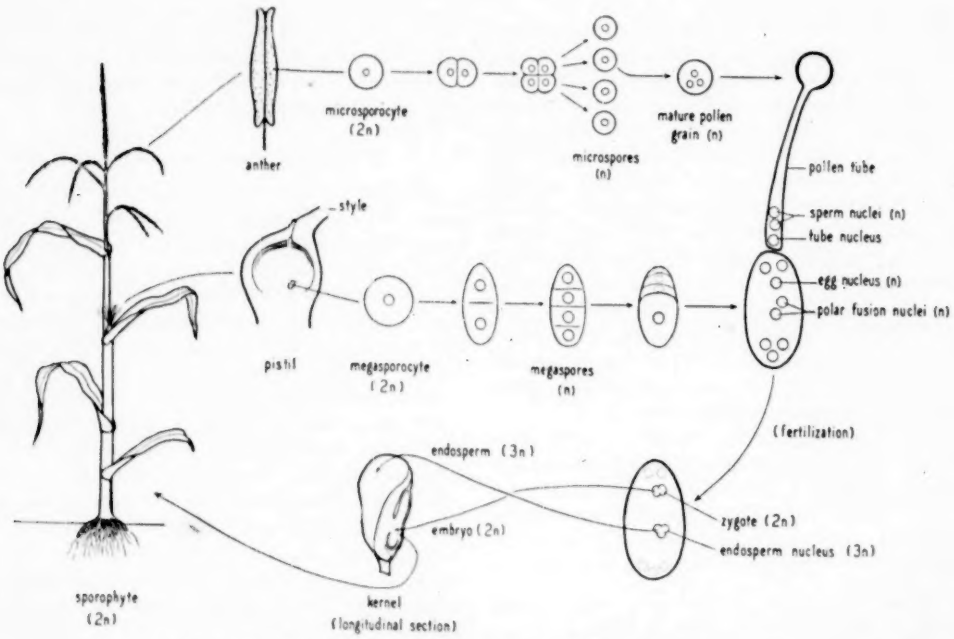


FIG. 1. *Life history of the corn plant (after Sturtevant and Beadle).*

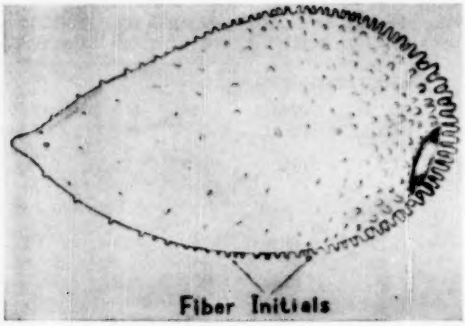


FIG. 2. *Diagram of young cotton seed on day of blooming, showing fiber initials (after Berkley).*

pure-breeding or homozygous plants or by cross-pollinating like parents, the resulting offspring will be like the parents. However, if heterozygous plants are self-pollinated or if unlike plants are cross-pollinated, the second-generation plants will be of different kinds, owing to the segregation and recombination of the chromosome pairs. The breeder depends upon new combinations as a means of producing improved varieties.

The obtaining of new combinations of characteristics may be illustrated by crossing two varieties of cotton, one of which is characterized by red plant color and white lint and the other by green plant color and brown lint. The first-generation plants are intermediate red in plant color and intermediate brown in lint color. If these plants are self-pollinated, the following generation will contain plants with different combinations of leaf and lint colors, including two new and pure-breeding combinations: (1) green plant and white lint and (2) red plant and brown lint.

## 2. Origin and Development of the Cotton Fiber

The seed of the cotton plant is developed through the combination of male and female gametes in the same manner as the kernel of corn illustrated in Figure 1.

Forty to 50 ovules are borne in the ovary and the pollen grains are borne in anthers or filaments attached to the staminal column which surrounds the ovary. On the morning that the flower opens, pollen grains reach the projecting stigma that extends above the ovary. The grains germinate and the tubes grow down to the ovules. The fertilized ovules develop into seeds. Some of the epidermal cells of the seed elongate into cotton fibers. Thus each cotton fiber is a single extended epidermal cell. The elongation of the epidermal cells begins the day that the flower opens and continues for 15 to 25 days. At the end of this period the fiber has attained its full length. A diagram of the cotton ovule on the day of flowering is shown in Figure 2. The length that the fiber finally reaches, as well as the amount of time required to attain this length, depends upon the variety and upon the environmental conditions. When the full length is reached, the second phase, or secondary-wall thickening, begins. Deposition of the secondary wall in most varieties takes place within a period of 25 to 40 days.

## 3. Effect of Inheritance and Environment on the Characteristics of Cotton Fiber

The quality of fiber produced by a cotton plant is determined by the inherent factors and by the environmental influences under which the plant grows. It has been said that a plant really inherits the ability to react in a given manner to a given set of environmental conditions. It is equally appropriate to say that environment plays the cards dealt by heredity.

If a group of distinct varieties are grown at the same location and under identical conditions, there will be a marked variation in fiber properties and these differences will be reflected in yarn strengths.

Variations in soil moisture, soil temperature, soil nutrients, and other environmental influences, such as the occurrence of insects and diseases during the development of the fiber, affect the expression of inherent factors.

The Division of Cotton and Other Fiber Crops and Diseases of the U. S. Department of Agriculture made a study of the effect of variety and environment upon the fiber characteristics of 16 varieties of cotton grown at 8 locations for 3 years.* The average skein strengths for varieties varied from 73 to 120 lbs. and the average skein strengths for locations varied from 80 to 104 lbs. Fiber strength variations for varieties were from 72,000 to 88,000 lbs. and for locations were from 72,000 to 87,000 lbs. Upper-quartile length variations for varieties were from 0.84 to 1.34 in. and for locations were from

* Anon. "Better Cottons," U. S. Department of Agriculture, Agricultural Research Administration, Bureau of Plant Industry, Soils, and Agricultural Engineering, Division of Cotton and Other Fiber Crops and Diseases, Beltsville, Md., 1947, pp. 895–964. (Illus.)

TABLE I. SUMMARY OF FIBER AND SPINNING TEST DATA FROM TESTS CONDUCTED WITH 8 STRAINS OF COKER 100 WILT BY THE U. S. DEPARTMENT OF AGRICULTURE

| | Sample identification | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 47-345<br>47-S-9 | 47-368<br>48-S-10 | 47-446<br>48-S-11 | 47-578<br>48-S-12 | 47-59-612<br>48-S-13 | 47-70<br>48-S-14 | 47-8134<br>48-S-15 | 47-120<br>48-S-16 |
| Grade | M from SM | SM from GM | SM | GM | GM | GM | GM | M |
| Staple length (in.) | 1 1/32 | 1 1/32 | 1 1/32 | 1 1/16 | 1 1/16 | 1 1/16 | 1 1/32 | 1 1/16 |
| Length (Fibrograph): | | | | | | | | |
| Upper-half mean (in.) | 1.08 | 1.09 | 1.14 | 1.10 | 1.09 | 1.10 | 1.06 | 1.11 |
| Mean (in.) | .84 | .84 | .86 | .88 | .85 | .89 | .84 | .85 |
| Uniformity ratio | 78 | 77 | 75 | 80 | 78 | 81 | 79 | 77 |
| Waste: | | | | | | | | |
| Picker and card (%) | 7.21 | 7.65 | 7.57 | 7.37 | 6.24 | 7.62 | 8.62 | 9.60 |
| Neps (per 100 sq. in. of card web) | 19 | 26 | 16 | 11 | 13 | 15 | 14 | 13 |
| Yarn strength and appearance: * | | | | | | | | |
| Carded 22's | 111.6B | 127.4B | 125.8C+ | 126.4B+ | 123.7B | 130.3B | 112.0B | 111.7B |
| Long-draft 36's | 62.5C+ | 70.8C+ | 71.4C+ | 69.3B | 68.3C+ | 72.5B | 62.4C+ | 61.3C+ |
| Processed 60's | 32.0C+ | 36.6C | 38.0C | 35.7C+ | 35.3C+ | 38.4C+ | 32.3C+ | 32.4C |
| Average index all yarn counts | 103.8 | 110.4 | 111.7 | 112.1 | 110.4 | 117.9 | 104.2 | 100.0 |
| Equivalent staple length, average (in.) | 1 1/32 | 1 1/16 | 1 1/16 | 1 1/32 | 1 1/32 | 1 1/32 | 1 1/32 | 1 1/16 |

* The figure is the strength (lbs.) and the letter is the yarn-appearance grade.

0.99 to 1.13 in. Although a given variety of cotton, when grown at several locations, is invariably stronger at a certain location, the relative strength of a group of varieties is about the same at all locations. For example, if variety A is stronger than variety B when grown in Alabama, it will also be stronger than variety B when grown in Texas.

Fortunately for the cotton breeder, heredity has a greater effect upon most of the fiber properties than does environment. Thus, variety is the most important single factor in determining the quality of fiber and the breeder can work with the assurance that breeding efforts can result in improved quality.

The most serious obstacle in the breeder's program is that frequently, if not usually, the varieties which possess the best fiber properties are not practical to produce because of low yields, low gin turn-out, late maturity, poor picking quality, or lack of resistance to disease. The breeder, however, has attained considerable success in overcoming these obstacles and is encouraged to continue his all-out efforts. These apparent correlations or antagonisms are occasionally being broken. Although the best fiber properties have not, as yet, been incorporated into a practical variety, breeders have succeeded in producing cottons with improved fiber characteristics and satisfactory agronomic characteristics.

## 4. Use of Fiber Technology in the Improvement of Fiber Quality Through Breeding

Two decades ago the cotton breeders drew on their knowledge, training, and acquired or inherited art and employed laboratory techniques to develop improved varieties. Excellent varieties of cotton serve as monuments to their splendid work. They sought to isolate from their breeding stocks new varieties that represented improvements in yield, gin turn-out, staple length, boll size, picking quality, stormproofness, earliness, disease- and insect-resistance, and regional adaptation. Statistical information for each of these characteristics was obtained and the data were analyzed in the most detailed manner. The results were used in selecting and discarding lines, in deciding which varieties would be released for farmer planting, and in measuring the progress made toward attaining certain goals that had been set.

At the present time the leading cotton breeders, in addition to employing these methods and techniques, are making full use of fiber technology in their breeding programs. The establishment of the Fiber Testing Service of the U. S. Department of Agriculture, with offices and laboratories in Washington, D. C., Clemson, South Carolina, Stoneville, Mississippi, and College Station, Texas, made available to the breeders for the first time facilities for obtaining

TABLE II. SUMMARY OF FIBER AND SPINNING TEST DATA FROM TESTS CONDUCTED WITH 4 STRAINS OF STONEVILLE 2B BY THE U. S. DEPARTMENT OF AGRICULTURE

| | Sample identification | | | |
|---|---|---|---|---|
| | C-101 | C-104 | C-107 | C-108 |
| Grade | SLM | SLM– | M | M |
| Staple length (in.) | $1\frac{1}{16}$ | $1\frac{1}{32}$ | $1\frac{1}{16}$ | $1\frac{1}{16}$ |
| Length (Fibrograph): | | | | |
| Upper-half mean (in.) | 1.08 | 1.03 | 1.11 | 1.05 |
| Mean (in.) | .84 | .82 | .89 | .84 |
| Uniformity ratio | 78 | 80 | 80 | 80 |
| Strength: Flat bundle (1,000 lbs./sq.in.) | 83,000 | 86,000 | 87,000 | 84,000 |
| Fineness: Weight (mg.) per in. | 4.2 | 3.8 | 4.5 | 4.2 |
| Waste: Picker and card (%) | 9.44 | 9.39 | 8.24 | 9.52 |
| Neps (per 100 sq. in. of card web) | 10 | 7 | 3 | 12 |
| Yarn strength and appearance: * | | | | |
| Carded 22's | 123.3B | 115.1B | 131.6B+ | 118.7B+ |
| Long-draft 44's | 50.6C+ | 47.5C+ | 55.8B | 50.1C+ |
| Processed 60's | 32.7C+ | 29.1C | 36.8C+ | 32.3B |
| Average index all yarn counts | 106.0 | 101.2 | 116.4 | 103.9 |
| Equivalent staple length, average (in.) | $1\frac{1}{8}$ | $1\frac{1}{32}$ | $1\frac{1}{16}$ | $1\frac{1}{16}$ |

* The figure is the strength (lbs.) and the letter is the yarn-appearance grade.

information on the physical properties of the fiber produced by their breeding stocks. These services have made possible the large and rapid gains in the quality of fiber of the American cotton crop, and these remarks are very inadequate as a tribute to the splendid work that these laboratories are doing. Every year laboratories are being installed by cotton mills, cotton brokers, commercial testing companies, and the breeders themselves. The number of samples from breeders' stocks being tested annually runs into hundreds of thousands. Thus the breeder in his modern program obtains, in addition to knowledge concerning the agronomic characteristics of his cottons, data on the tensile strength of fiber, the upper half and mean fiber lengths, length uniformity, fineness, maturity, yarn strength, yarn grade, picker and card waste, and mill performance.

In Tables I and II examples of the type of fiber data obtained in a cotton breeding program are given. These data are used to show how selection within a commercial variety may result in obtaining a new variety that possesses much better fiber quality than does the parent strain.

Table I * is a copy of the Summary of Fiber and Spinning Test Data obtained in tests made by the U. S. Department of Agriculture with 8 strains of the variety Coker 100 Wilt. Attention is called to samples 47–368, 47–446, 47–578, 47–59–612, and 47–70. These lots have exceptionally high yarn strength and consequently equivalent staple lengths that are considerably longer than the actual length of the respective samples.

A Summary of Fiber and Spinning Test Data obtained by the U. S. Department of Agriculture in tests with 4 lots of cotton from breeding stocks of the Stoneville Pedigreed Seed Company is given in Table II. Sample C-101 was produced by the parental variety from which new lines C-104, C-107, and C-108 were selected. The outstanding progeny of this group is number C-107, which has a classers' length of $1\frac{1}{16}$ in. and an equivalent length of $1\frac{3}{16}$ in. This represents an improvement over the parental variety, which itself is an outstanding cotton with an equivalent length of $1\frac{1}{8}$ in. Strain C-107 is better than its parental line with respect to length uniformity, fiber strength, picker and card waste, nep count, yarn strength, and yarn appearance. The new strain is outstanding in yield and in stormproofness.

For several decades plant breeders have sought to develop varieties of cottons that would produce strong, high-count yarns. To accomplish this they have selected strains with increased staple lengths and finer fibers. Although outstanding accomplishments have been made in this type of program, unfortunately these cottons have consistently yielded less than the medium- and short-staple uplands and have been characterized by low gin turn-out. In the

* The writer is indebted to Dr. George J. Wilds of the Coker's Pedigreed Seed Company for the data given in Table I.

breeding program of the U. S. Cotton Field Station at Stoneville, Mississippi, a strain of Deltatype Webber was isolated which had a classers' length of 1½ in. and an equivalent length of 1⅛ in. This cotton was coarser than varieties of the same equivalent staple length and it had a bundle strength of 94,300 lbs. and a yarn-appearance grade of B −. It was outstanding in mill performance in as much as no ends-down in combed 100's occurred in the spinning test. The Deltatype Webber was grown in a planting with a leading 1⅛-in. cotton. The commercial strain had a bundle strength of 89,100 lbs., 13.3 ends-down per 100 spindles per hr. for combed 100's, a yarn-appearance grade of C, and a considerably lower yield than the new Deltatype Webber strain.

The development of this new strain illustrates the possibility of obtaining a variety of cotton with high yarn strength even though the fiber is relatively short. Medium-long-staple, strong-fiber cottons would be expected to have higher yields and better lint percentages than the long-staple cottons which in the past have been the source of the stronger yarns.

### 5. Technique of Improving Cotton Through Breeding

There are two popular, mistaken beliefs regarding the development of improved varieties of cotton. One of these is that improved cottons are developed through mysterious methods by wizards possessing supernatural powers; the other is that the better varieties are chance findings by breeders who "lucked up" on them. The remainder of this paper will be devoted to the procedures followed in a general cotton breeding program, which should reveal that, in reality, a cotton breeder uses cotton plants and employs breeding techniques in much the same manner that a construction engineer uses his materials and methods.

There are five steps in the cotton breeder's program: (1) obtaining stocks, (2) isolating lines, (3) testing strains, (4) increasing seed stocks, and (5) distributing planting seed to farmers.

After the breeder knows the type of cotton that he wishes to develop, he next obtains the stocks with which to work. This material is generally from one of four sources: (1) open-pollinated stocks, (2) line-bred stocks, (3) inbred lines, or (4) new, controlled hybrid combinations.

Commercial varieties are the most common source of open-pollinated stocks. These have been grown for a few to many years, with no effort to prevent brother-sister crosses. If they have been out of the hands of breeders for several years, there is always a probability that considerable variation will occur because of cross-pollination. These variations offer excellent opportunities for the selection of new combinations of characteristics. Line-bred stocks are strains that are obtained by reselection in the intermediate steps in the developing of the varieties. New, controlled hybrid stocks represent an effort on the part of the breeder to incorporate into one stock most of the desirable characteristics of two or more varieties and at the same time to eliminate as many as possible of their undesirable characteristics.

The procedure of isolating lines and the subsequent steps are outlined in Figure 3. Let us assume that one step is made in each of 8 consecutive years, the breeder having started in 1948 with 1,000 plant selections.

Individual plants are selected on the basis of every characteristic that can be determined in the field, such as yield, plant type, amount of foliage, foliage pubescence, type of bract, boll size and shape, hand- and machine-picking qualities, earliness, staple length, disease- and insect-resistance, and stormproofness. Determination of approximate fiber strength and fineness, length uniformity, and gin percentage may also be made by the veteran breeder.

In 1949 the seed from each plant is planted in a progeny row, approximately one-hundredth acre in size. During the season the plant breeder observes each row, attempts to determine the degree of uniformity between plants, and makes a careful study of the various characteristics. In addition, some rough determinations of fiber properties are made visually. On the basis of all the determinations, about 900 of the rows are discarded; the remaining 100 are harvested and kept separately. Before the entire production is picked, a sample of 100 bolls is taken for an accurate determination of boll size. For all of the cotton from each "saved" row laboratory determination is made of gin turn-out, staple length, lint index, seed index, fiber strength, length uniformity, and fineness. Seed samples are analyzed for their oil-mill value. On the basis of these laboratory determinations, about 50 of the 100 selected rows are discarded.

In 1950 the seed from each saved progeny row will be divided into two portions. One part will be planted in a ¼-acre increase plot. The other will

be planted in a replicated yield trial. These two plantings will provide an increase in the quantity of seed and data from precise tests for statistical analyses. Notes will be made on uniformity between plants, plant type, amount of foliage, foliage pubescence, type of bract, boll size and shape, ease of picking, disease- and insect-resistance, and stormproofness. By making measurements and analyzing the data obtained, the strains may be compared in regard to yield, earliness, staple length, gin turn-out, lint index, seed index, fiber strength, length uniformity, fiber fineness, and seed grade. Spinning samples will be sent to spinning laboratories for determination of yarn strength, yarn appearance, equivalent staple length, waste, and probable mill performance. On the basis of all the data obtained from

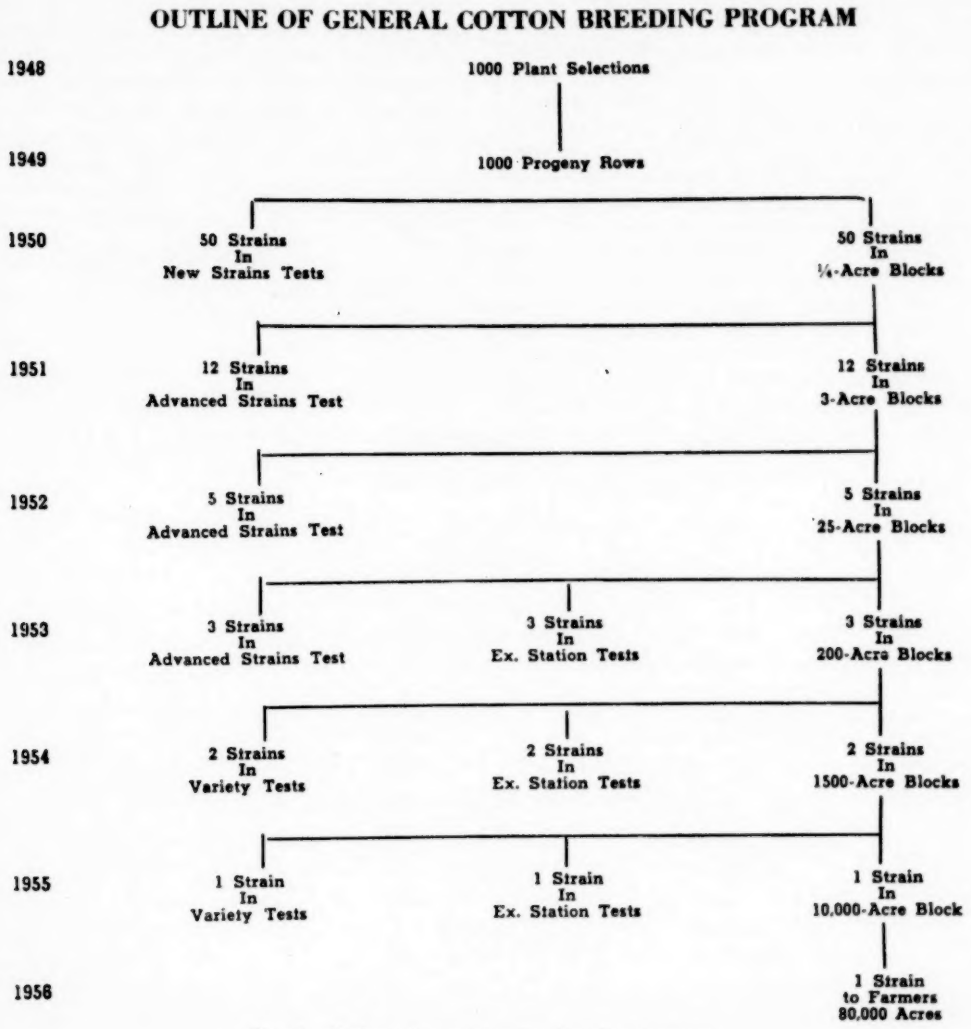


FIG. 3. *Outline of general cotton breeding program.*

field and laboratory, approximately 12 strains will be saved and the rest discarded. Seed from the increase blocks will be used for further testing and increasing. Seed from the strains test will be discarded.

In 1951, 12 strains will be planted in an advanced strains test and each strain will be planted in a 3-acre increase field. The same information as for the 1950 new strains test will be obtained. The results from the two tests will be used to determine the strains that should be saved for further testing and increasing. On the average, about 5 strains will be continued.

In 1952, these 5 strains will be planted in an advanced strains test and the supply of seed from each strain will be increased in a 25-acre field. Information similar to that for the previous 2 years will be obtained and on the basis of the results of the 3 years of testing about 3 strains will be saved.

These 3 strains will be planted in advanced strains tests conducted by the breeder at different locations and by agricultural experiment stations that are interested in getting advance information on forthcoming varieties. At the same time each of the 3 strains will be planted in a 200-acre block. Observations in the field and tests in the laboratories will be made as they were for the 3 preceding years. At this stage the breeder will probably desire that a mill test be made with a large number of bales of each of the strains. On the basis of the results from the 4 years of testing, one of the 3 strains will probably be discarded.

In 1954 the 2 surviving strains will be planted in the breeder's variety tests and in tests conducted by experiment stations. A 1,500-acre increase of each strain will be planted. The regular field observations and laboratory tests will be repeated and again mill tests will be desired. Probably 1 of the 2 strains will be discarded after all the available data from the 5 years of testing are compiled.

The remaining strain will be planted in 1955 in several variety tests conducted by the breeder and by the experiment stations in order that farmers may have up-to-date information on the performance of the strain. During the same season seed will be increased on approximately 10,000 acres, and the following winter these will be released to certified seed growers and to other farmers for planting on approximately 80,000 acres.

That is the history of the developing of a new variety of cotton from one-half pound of seed in the harvest of 1948 to 40,000 tons in the harvest of 1956.

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